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INORGANIC COLLOID CHEMISTRY

BY PROFESSOR HARRY B. WEISER

INORGANIC COLLOID CHEMISTRY

Vol I The Colloidal Elements.
389 pages 6 by 9 54 figures Cloth

Vol II. The Hydrous Oxides and Hydroxides.
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Vol. III. The Colloidal Salts.
473 pages 6 by 9 74 figures Cloth

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INORGANIC COLLOID CHEMISTRY

BY

HARRY BOYER WEISER

Professor of Chemistry at The Rice Institute

VOLUME III

THE COLLOIDAL SALTS

NEW YORK

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PREFACE

This book is the last in a three-volume treatise on inorganic colloid chemistry which deals with the colloidal behavior of the elements and their inorganic compounds. Like the two preceding books, The Colloidal Elements (1933) and The Hydrous Oxides and Hydroxides (1935), this volume, entitled The Colloidal Salts, is concerned primarily with the contributions that have been made to the theories and applications of colloid science from observations on inorganic substances. The importance of the salts in the study of colloidal phenomena is evidenced by the amount and character of the work that has been carried on with this class of compounds during the past decade. So significant are the results of the investigations that a book on this subject written by the author and published by the McGraw-Hill Book Company ten years ago had to be completely revised and almost entirely rewritten in the preparation of the present volume.

The plan of the book is similar to that followed in the first two volumes of the series. After an introductory chapter dealing with the general methods of formation of gels and sols of the salts, separate sections are devoted in turn to the colloidal sulfates; colloidal carbonates, phosphates, chromates, and arsenates; colloidal halides; colloidal sulfides; colloidal ferrocyanides and ferricyanides; and colloidal silicates. The first portion of each section is concerned with a critical survey of the conditions of formation and the general characteristics of the individual salts in the colloidal state; and the second portion, with the principles underlying their applications.

Among the examples of colloid chemical behavior that have received special consideration in this volume are: the velocity of precipitation and the physical character of precipitates; the stability of sols and the mechanism of the electrolyte coagulation process; ion antagonism in colloid systems; the mutual coagulation process; adsorption on ion lattices; adsorption indicators; the color of colloids; the permeability of membranes; and the phenomena of thixotropy and rheopexy.

The principles underlying the technical applications of the colloidal salts are illustrated by chapters on: plaster of Paris; lithopone

and other sulfide pigments; Prussian blue; the colloidal halides in photography; the base-exchange phenomenon in silicate gels; the inorganic colloids of the soil; and Portland and aluminous cements.

Following the practice of the earlier volumes of the treatise, the attempt is made to render this critical survey of the colloidal behavior of the salts as clear and concise as possible by the generous use of section and paragraph headings in bold-face type. It is hoped that this outline of the subject matter will contribute to the usefulness of the book both for reference purposes and as a textbook for the study of the principles of colloid chemistry in connection with a well-known and widely diversified class of inorganic compounds.

August 10, 1937 HARRY BOYER WEISER.

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THE COLLOIDAL SALTS

CHAPTER I

INTRODUCTION

Thomas Graham[1] in his fundamental paper "Liquid Diffusion Applied to Analysis" showed that substances like certain inorganic salts, sugar, and glycerol, which are readily obtained in a crystalline form, will diffuse through water and certain membranes much more rapidly than substances such as albumin, gelatin, and the hydrous oxides which are gelatinous in character and are obtained in the form of crystals with difficulty, if at all. Substances which diffused rapidly were called crystalloids, and those which showed little or no diffusion were termed colloids, from the Greek word for glue. On the basis of this distinction most inorganic salts would not be classified as colloids; but Graham recognized that the classification was arbitrary. The important investigations of von Weimarn[2] with a definitely crystalline inorganic salt, barium sulfate, confirmed the view that the distinction between crystalloids and colloids is not tenable and that we should speak of a colloidal state of matter, a concept first recognized by Graham. A material is said to be colloidal when it is sufficiently finely divided, the diameters of the dispersed particles ranging from approximately 100 mμ to 1 mμ.[3] Since a large number of the inorganic salts are readily obtained in the colloidal state of subdivision, investigations with this class of substances have played an important part in the development of colloid chemistry both theoretical and applied. Attention will first be given to the general conditions for forming colloidal inorganic salts.

[1] Phil Trans, **151**, 183 (1861)

[2] Kolloid-Z., **2**, 199, 230, 275, 301, 326, suppl. 2 LII; **3**, 89, 282 (1908); **4**, 27 (1909); "Grundzuge der Dispersoidchemie" (1911); "Zur Lehre von den Zustanden der Materie" (1914).

[3] Ostwald, Wo.: "Grundriss der Kolloidchemie" (1909).

Formation of Gels and Sols of Inorganic Salts

The two general methods for obtaining substances in the colloidal state are (1) condensation, in which smaller particles, molecules, or atoms are gathered into particles of colloidal dimensions, and (2) dispersion, in which the material in mass is dispersed into particles of colloidal dimensions.

Condensation Methods

Colloidal salts are obtained either in the form of gels—gelatinous precipitates and jellies—or sols. Condensation methods are far more important than precipitation methods in the preparation of both these types of colloidal systems. Indeed, as we shall see, the most common examples of dispersion methods of forming colloidal salts actually start with aggregates of particles of colloidal dimensions which have been obtained by a condensation process.

Condensation methods as applied to the formation of colloidal salts usually involve precipitation as a result of chemical reactions in solution. Von Weimarn [2] made the first systematic investigation of the form in which substances precipitate as a result of reactions in solution and outlined the conditions under which sols and gels would be expected to form. The von Weimarn theory has been considered briefly in the earlier volumes of this work,[4] and its applicability and limitations will be taken up in detail in the next chapter, which deals with colloidal barium sulfate. For the present it need only be pointed out that particles of colloidal dimension will precipitate when the percentage supersaturation is sufficiently high at the moment precipitation begins. The percentage supersaturation is defined by the expression $(Q - L)/L$, where Q is the total concentration of the substance that will precipitate and L is its solubility. In general, a highly insoluble substance precipitates in the colloidal state as a sol, a gelatinous precipitate, or a jelly depending on the concentration of the reacting substances [$(Q - L)/L$ is large because L is very small]. Fairly soluble substances, on the other hand, come down in the gelatinous or jelly-like form only from highly concentrated solutions [$(Q - L)/L$ is large because Q is very great].

Von Weimarn emphasized that substances thrown down in the form of gels pass through the sol state at some stage of the process. This means that a gel results from the agglomeration of a sol that may have but a transient existence or that may be quite stable in the ab-

[4] Vol. I, pp. 1-4, 26-28 (1933); II, p. 3 (1935).

sence of excess electrolyte (Vol. II, p. 15). From this point of view, the problem of the synthesis of stable sols is to create conditions such that the sol state is maintained for an indefinite period. The von Weimarn theory tells us only that very low solubility of the precipitating phase and high dilution favor sol formation. In actual practice, precipitation in the form of particles of colloidal dimensions is effected and coagulation or agglomeration of the colloidal particles is prevented in one of two ways: (1) keeping down the concentration of coagulating electrolyte by choosing a suitable reaction or by dilution, or (2) adding protecting agents such as "water-soluble" protecting colloids which are adsorbed on the surface of the particles and prevent their coming in contact. The most typical reaction for the preparation of metallic sols is reduction, for the preparation of hydrous oxide sols is hydrolysis, and for the formation of sols of the inorganic salts is double decomposition. The general methods of forming salt sols together with some specific illustrations will be taken up in order.

Double Decomposition in Which the Second Product Is a Nonelectrolyte. Since sols are coagulated by electrolytes above a certain concentration, it follows that the preparation of stable sols by double decomposition depends to a large extent on the second product of the reaction. If the reaction is chosen so that the second product is a nonelectrolyte or a weakly dissociated electrolyte, the conditions will be favorable to sol formation. The classical example under this heading is the reaction between hydrogen sulfide and a solution of arsenious acid: $2H_3AsO_3 + 3H_2S \rightarrow As_2S_3 + 6H_2O$.[5] The electrolyte concentration is quite low throughout the process, and the sulfide remains dispersed as negatively charged particles stabilized by the preferential adsorption of S^{--} and HS^- ions. In this case the conditions for sol formation are so favorable that the sol can be made as concentrated as 3 g of As_2S_3 per 5 g of water.[6] Similarly, a stable sol of mercuric sulfide is formed by the interaction of a saturated solution of mercuric cyanide and hydrogen sulfide[7] since hydrocyanic acid, the second product of the reaction, is so weakly dissociated; copper glycocoll treated in a similar way yields a stable cupric sulfide sol.[7]

Double Decomposition in Which the Second Product Is an Electrolyte. Because of the coagulating action of electrolytes, a stable sol

[5] Berzelius: "Lehrbuch der Chemie," 3rd ed. (1834).
[6] Schulze: J. prakt Chem., (2) **25**, 431 (1882).
[7] Lottermoser: J. prakt. Chem., (2) **75**, 293 (1907).

results when the second product of the double decomposition is an electrolyte, under one of the following conditions: (1) very high dilution, (2) one of the electrolytes contains an ion which is adsorbed very strongly by the dispersed particles. As an example of the first, sols of most of the metallic sulfides are obtained by the interaction of very dilute solutions of the respective chlorides and hydrogen sulfide.[8] The classical example of the second is the observation of Lottermoser[9] that at sufficiently low concentrations silver halide sols result from the interaction of silver nitrate and alkali halide provided that one or the other of the reactants is in slight excess. With the silver salt in excess the particles are positively charged by reason of preferential adsorption of silver ion; with the halide in excess the particles are negatively charged because of preferential adsorption of halide ion. This stabilizing effect of the adsorbed ions is greater than the coagulating action of alkali nitrate, the second product of the metathetical reaction

Double Decomposition in the Presence of Strongly Adsorbed Non-electrolytes. The precipitation of salts is frequently prevented from going beyond the colloidal range and the dispersed phase kept in the sol state by the addition of substances which are strongly adsorbed such as the so-called protecting colloids and sugar or glycerol. Thus, concentrated stable sols of silver halides and Prussian blue are obtained by precipitation in the presence of gelatin.[10] Silver sulfide and cadmium sulfide are stabilized in the sol state by gum arabic or casein.[11] Silver chromate remains as a sol in the presence of sugar; and most insoluble salts can be held in colloidal solution by sodium "protalbinate" and "lysalbinate" which are formed by the saponification of albumin.[12] Sodium chloride resulting from the interaction of sodium malonic ester and chloroacetic ester in dry benzene is stabilized in the sol condition by strong adsorption of one or more of the organic reagents.[13] Barium sulfate thrown down from aqueous alcohol gives a gel which forms a sol on shaking with a larger quantity of water.[14] Strong adsorption of alcohol doubtless helps to prevent both coalescence and growth of the dispersed particles since a jelly

[8] Winssinger: Bull. soc. chim., (2) **49**, 452 (1888).
[9] J. prakt. Chem., (2) **68**, 341 (1903); **72**, 39 (1905); **73**, 374 (1906).
[10] Lobry de Bruyn: Rec. trav. chim., **19**, 236 (1900).
[11] Müller and Artmann: Oesterr. Chem.-Ztg., **7**, 149 (1904)
[12] Paal: Ber., **39**, 1436; Paal and Kühn: 2859, 2863 (1906); **41**, 51, 58 (1908).
[13] Michael: Ber., **38**, 3217 (1905).
[14] Kato: Mem. Coll. Sci, Kyoto Imp. Univ, **2**, 187 (1909).

thrown down from aqueous solution does not give a stable sol on shaking with water.

A special case under this heading is the sols in concentrated electrolyte solutions. For example, colloidal sulfides and silver halides may be prepared by double decomposition in concentrated sulfuric acid or phosphoric acid.[15] The particles in such sols are without charge; the stability results from strong adsorption of the dispersion medium. It thus appears that a hydrophobic sol of a given charge has two stable and two unstable zones depending on the electrolyte concentration. With little or no electrolyte such sols are unstable; with a small electrolyte concentration they are stable; somewhat larger concentrations cause flocculation; and finally very high concentrations again exert a stabilizing influence.

Replacement of Solvent. In this general method of sol synthesis, a solution of the substance under consideration is poured into a liquid in which the solute is so insoluble that it appears as a highly dispersed phase. This procedure is of limited applicability in the synthesis of sols of the inorganic salts, and one example will suffice. Silver iodide is insoluble in water but is fairly soluble in a solution of potassium iodide.[16] When a solution of the salt is poured into a large volume of water, a silver iodide sol is formed stabilized by the preferential adsorption of iodide. High dilution is essential to avoid an excess of potassium iodide which would cause coagulation.

Oxidation. Certain salts have been obtained in the colloidal state by the oxidation of the corresponding metallic sols. Thus silver halide sols are obtained by the action of chlorine, bromine, and iodine, respectively, on a silver sol[17] until the characteristic color of the metallic sol is destroyed. The stability of the resulting halide sols is increased by the presence of gelatin or ammonium citrate. A similar procedure may be employed to prepare the more insoluble halide sols of lead and mercury.

Dispersion Methods

Dispersion methods of preparing sols involve the washing out of a precipitating agent, the addition of a peptizing agent, and disintegra-

[15] Voet: J. Phys. Chem., **40**, 307 (1936); Ostwald and Wannow: Kolloid-Z., **76**, 159 (1936).

[16] Hellwig: Z. anorg. Chem, **25**, 157 (1900).

[17] Lottermoser and Meyer: J. prakt. Chem., (2) **56**, 247 (1897); **57**, 543 (1898).

tion by electrical or other means. Each of these general procedures has been employed in preparing salt sols.

Washing Out of Precipitating Agent. When a precipitate consists of highly dispersed primary particles that have agglomerated into aggregates which settle out, it may be repeptized to the sol state by washing out the electrolyte responsible for the agglomeration. It should be emphasized that this procedure is applicable only if the material to be peptized already exists in the colloidal state of subdivision and if the particles do not grow as a result of solution of smaller grains and growth of larger ones at their expense (Ostwald ripening). The method has proved particularly useful in the direct preparation of fairly pure hydrous oxide sols, and it is applicable to the preparation of various kinds of salt sols. Thus zinc sulfide thrown down from chloride solution by ammonium sulfide is peptized in part by washing out the ammonium salt.[18] Copper ferrocyanide gel thrown down from alkali ferrocyanide solution with a small excess of copper salt is peptized if the copper salt is removed by washing.[19] By using hydroferrocyanic acid and cupric acetate to form the gel and washing by the aid of the centrifuge, a sol of almost any desired purity may be prepared.[20] Silver halides precipitated rapidly in the cold and washed at once by decantation undergo partial repeptization to the sol state.

Addition of Peptizing Agent. If the primary particles of a colloidal precipitate have coalesced sufficiently, the coagulation is not reversible by washing alone. Under such circumstances the particles may be broken apart once more by the addition of a suitable peptizing agent. The Prussian blue gel is readily peptized by oxalic acid, and freshly precipitated metallic sulfides are peptized by hydrogen sulfide. Similarly, a freshly formed silver halide gel is peptized by a small amount of either silver nitrate or alkali halide. Carbon dioxide passed into a solution of barium oxide in methyl alcohol gives at first a thick gel of barium carbonate which is peptized by the addition of more gas, forming an opalescent sol.[21]

Electrical Disintegration. The formation of sols by means of an electric arc under water or organic liquid is applicable chiefly to the preparation of metallic sols; but the method finds some application in

[18] Donnini: J. Chem. Soc., **66** (2), 318 (1894).

[19] Berkeley and Hartley: Phil Trans, **206A**, 486 (1906).

[20] Weiser and Milligan: J. Phys. Chem., **40**, 1071 (1936).

[21] Neuberg and Neumann: Biochem. Z., **1**, 166 (1906); Neuberg and Rewald: Kolloid-Z, **2**, 321 (1908).

the preparation of sols of certain salts, chiefly sulfides, which conduct the current fairly well. Von Hahn [22] prepared stable sols of galena, molybdenite, and antimonite [23] by cathodic disintegration with a direct-current arc as used by Bredig.[24] The dispersion of molybdenite takes place only when the temperature exceeds 53° more or less, the critical temperature varying slightly with different minerals. This appears to be the first recorded example of a critical temperature in the electrical synthesis of sols. The oscillatory discharge first used by Svedberg [25] to synthesize sols gives sols of antimonite, sphalerite, chalcocite, and molybdenite, whereas only coarsely dispersed systems are obtained with iron pyrites and galena.

The general conditions for obtaining salts in the colloidal state having been outlined, attention will be directed to the colloidal behavior of this important class of inorganic substances. It seems advisable to begin with colloidal barium sulfate since this compound illustrates so well the effect of the conditions of precipitation on the nature and form of the resulting precipitate

[22] Kolloid-Z. (Zsigmondy Festschrift), **36**, 277 (1925)

[23] *Cf.* Currie: J Phys. Chem., **30**, 205 (1926)

[24] Z. Elektrochem, **4**, 514 (1898); Bredig and Berneck Z physik Chem, **31**, 258 (1899).

[25] "The Formation of Colloids," 19 (1921).

Part I

THE COLLOIDAL SULFATES AND RELATED COMPOUNDS

CHAPTER II

COLLOIDAL BARIUM SULFATE

The Physical Character of Precipitated Barium Sulfate

The importance of barium sulfate in gravimetric analytical chemistry, is responsible for a large number of investigations into the conditions of precipitation of the salt and how these influence its physical character and properties. Von Wiemarn was the first to show that barium sulfate can be prepared in the laboratory in a variety of physical states from masses of distinct macrocrystals to transparent jellies The extended investigations of von Wiemarn on this and other related salts led to a theory of the precipitation process, the applicability and limitations of which will be considered in some detail.

Velocity of Precipitation and Growth of Particles

The Velocity Equations. In his systematic study of the conditions which influence the form of precipitates, von Weimarn[1] calls attention to a number of factors which may determine their nature: the solubility of the substance; the concentration at which precipitation takes place; the latent heat of precipitation; the normal pressure at the surface of the solvent; the molecular complexity of the reactants; polymerization of the reacting molecules; viscosity of the reaction medium; adsorption; the presence of dust particles; and the extent of agitation on mixing. Other important factors which he seems to have overlooked are the specific tendency of the reaction product to form nuclei and the specific tendency to grow on nuclei. Von Wiemarn recognized the impossibility of taking all these factors into account and simplified the problem at the outset by considering only the first two factors: the solubility of the precipitating substance and the concentration at which the precipitation starts. The precipitation process is considered as taking place in two stages: the first stage, in which

[1] Kolloid-Z., **2**, 199, 230, 275, 301, 326, suppl 2 LII; **3**, 89, 282 (1908); **4**, 27 (1909); "Grundzüge der Dispersoid Chemie" (1911); "Zur Lehre von den Zustanden der Materie" (1914); Repts. Imp. Ind Research Inst., Osaka, Japan, V, **8**, 7 (1927); **9**, 3 (1928); **12**, 5 (1931).

the molecules condense to invisible or ultramicroscopic nuclei; and the second, which is concerned with the growth on the nuclei as a result of diffusion. The velocity W at the important first moment of the first stage of the process is given by:

$$W = K\frac{\text{precipitation pressure}}{\text{precipitation pressure}} = K\frac{Q-L}{L} = K\frac{P}{L} = KU \qquad (1)$$

where Q is the total concentration of substance that is to precipitate; L, the solubility of coarse crystals; and K, a constant. P is the absolute supersaturation, and $P/L = U$ is the percentage supersaturation at the beginning of precipitation. To take care of all the other factors which may enter into the process von Weimarn introduces a "variable multiplier" J, and the equation becomes:

$$W = KJ\frac{Q-L}{L} \qquad (2)$$

The Nernst-Noyes equation gives the velocity, V, of growth on nuclei:

$$V = \frac{D}{S} \cdot O \cdot (Q-L) \qquad (3)$$

where D is the diffusion coefficient; S, the thickness of the adhering film (length of the diffusion path); O, the extent of surface; and Q and L have the same significance as above.

Several facts may be interpreted qualitatively by the aid of these equations: It will be seen that the velocity of the precipitation depends not on the supersaturation P, but on the percentage supersaturation P/L. Thus, with a given value of P (say, a few grams per 100 cc), a very soluble substance, such as sodium chloride, will deposit nothing at first and finally a few crystals may form; but with the same value of P, an almost insoluble substance, such as alumina or silver chloride, will give an immediate gelatinous or curdy precipitate. The difference is that the velocity of precipitation is much smaller in the first case than in the second. On the other hand, if sodium chloride is formed by the interaction of sodium ethylate or thiocyanate and hydrochloric acid in a mixture of ether and amyl alcohol in which sodium chloride is practically insoluble, the precipitate is curdy like that of silver chloride.

Although the value of P is not in itself of primary importance in determining the form of the precipitate, its value is not without influence, since quite different results are obtained depending on

whether a given value of U is obtained by a large P or by a small L. In the first instance, a large amount of the dispersed phase will be produced, and in the second, very little. Hence a large U-value resulting from a large value of P will, in general, give a gelatinous precipitate or a jelly; whereas a large U-value resulting from a very small L-value will give a large number of highly dispersed particles—a sol. It would appear, therefore, that the dispersed phase can be made to separate in any desired form by suitable alteration of P or L or of both.

Effect of Concentration of Reactants on the Precipitate Form. For sparingly soluble substances, von Weimarn distinguishes five stages with increasing supersaturation: If the supersaturation is slight, no precipitation occurs inside of several years; in the next stage of higher supersaturation, perfect crystals appear in a relatively short time; in the third stage, skeleton crystals and needles appear; in the fourth stage, gelatinous precipitates are formed; and in the highest stage of supersaturation, jellies result.

The observations of von Weimarn on barium sulfate illustrate the effect of concentration of reactants on the form of a precipitate. The concentration of this salt (0.0024 g/l at 18°) is fairly high compared to that of alumina, say; hence the values of P which can be obtained are not large enough to give large values of U, using the ordinary laboratory solutions of barium chloride or nitrate and alkali sulfate. With these reagents, the rate of formation of particles is relatively slow and their subsequent growth is rapid; hence the precipitate ordinarily obtained consists of fairly large crystals. But by making use of more soluble salts, such as barium thiocyanate or iodide and ammonium or manganese sulfate, it is possible to obtain the salt in any form from large crystals to a clear jelly. In the actual experiments, equivalent solutions should be mixed in equal volumes; it is necessary, of course, to use correspondingly large volumes of the very dilute solutions, otherwise there will not be a visible quantity of barium sulfate to separate out. Strictly, the product of the volume and concentration should be constant. The results of a series of observations are given in Table I. It is obvious from these data that a barium sulfate sol cannot be obtained unless L is diminished since increasing the value of P to the point where colloidal particles are formed gives a gel. Actually Kato [2] obtained a sol in the presence of alcohol in which barium sulfate is much less soluble than it is in water. Kato also obtained much more stable gels by the interaction of

[2] Mem. Coll. Sci., Kyoto Imp. Univ., **2**, 187 (1909).

TABLE I

EFFECT OF CONCENTRATION OF REACTANTS ON THE PHYSICAL CHARACTER OF BARIUM SULFATE (L = 0.002 g/l)

Normality of $Ba(CNS)_2$ and $MnSO_4$	P	$U = \frac{P}{L}$	Nature of precipitate
0 00005 to 0 00014	0 000 to 0 006	0 to 3	No precipitate in a year. Microcrystals would be expected in a few years and macrocrystals from large amounts of solution.
0 00014 to 0 0017	0 006 to 0 096	3 to 48	Slow precipitation at U = 8. Momentary sol stage at U = 25. Complete separation in months to hours.
0 0017 to 0 75	0 096 to 43.8	48 to 21,900	Crystal skeletons and needles precipitate in a few seconds at U = 48, beyond this, instantaneous precipitation. Crystals barely recognizable at U = 21,900.
0 75 to 3 0	43 8 to 175 1	21,900 to 87,500	Precipitates which appear amorphous, form immediately.
3 0 to 7 0	175 1 to 409 0	87,500 to 204,500	Clear cellular jellies.

barium and sulfate ions in alcohol-water mixtures. Similarly, Lehner and Taylor [3] prepared stable gels by the interaction of dilute solutions of barium chloride and sulfuric acid in selenium oxychloride in which barium sulfate is almost entirely insoluble. Careful observations disclosed that selenium oxychloride is without action on polished surfaces of barite and does not penetrate barium sulfate crystals. The evidence appears conclusive, therefore, that gelatinous barium sulfate obtained in selenium oxychloride is merely barium sulfate made plastic by adsorbed selenium oxychloride. This accords with the author's view [4] that a gelatinous precipitate consists of very finely divided solid particles which have adsorbed the liquid strongly. The greater stability of the alcogels and selenium oxychloride gels, as compared with the

[3] J. Phys. Chem., **28**, 962 (1924).

[4] Weiser: Bogue's "Colloidal Behavior," **1**, 389 (1924); *cf.* Vol. II, p 14.

aqueous gels, results both from lower solubility of barium sulfate in the organic liquids and from stronger adsorption of the organic liquids than of water. This is not true of all organic liquids: when barium sulfate is shaken with a mixture of water and heptane the salt concentrates in the dineric interface, indicating that the adsorption of the two liquids is of the same order; on the other hand, when the salt is shaken with a mixture of heptane and selenium oxychloride, it concentrates in the selenium oxychloride layer, and when shaken with a mixture of selenium oxychloride and 70% H_2SO_4, it collects in the acid layer.

The Precipitation Laws

Von Weimarn[5] formulated the following precipitation laws as a result of observations on the precipitation of various salts such as the sulfates of barium, strontium, calcium, and silver from aqueous and aqueous-alcoholic solutions:

1. With increasing concentrations of reacting solutions, the average size of the precipitated individual crystals (not their aggregates) passes through a maximum during the process of direct crystallization.

2. With increasing concentrations of reacting solutions, the size of the crystals decreases continuously after the completion of the process of direct crystallization.

3. For the same absolute concentrations ($Q - L$) of reacting solutions, other conditions being equal, the average size of the precipitated crystals decreases with decreasing solubility of a substance.

4. With increasing viscosity of the dispersion medium, the average size of the particles decreases.

The first three laws may be represented schematically in Fig. 1, in which the effective concentration of reacting solutions ($Q - L$) or the velocity of precipitation is plotted against particle size for three solubility values, L', L'', and L''', which yield, respectively, macroscopic, microscopic, and ultramicroscopic crystals. The L_A-curves represent the first law; the L_B-curves, the second; and the positions of the L_A-curves and L_B-curves with respect to each other, the third. In general, the L_A-type of curve showing a maximum is obtained a short time—15 to 30 seconds—after the mixing, and the L_B-type a month or more after the mixing. The L'-curves are obtained from a medium in which the substance is fairly soluble, for example, barium sulfate precipitated from hot hydrochloric acid solution; the L''-curves cor-

[5] *Cf.* Chem. Rev., **2**, 217 (1926); Alexander's "Colloid Chemistry," **1**, 27 (1926).

respond, for example, to the precipitation of barium sulfate from aqueous solutions; and the L'''-curves to the precipitation from aqueous alcoholic solutions. With 40% alcohol and higher, the curves for barium sulfate lie almost entirely in the ultramicroscopic zone.

Contrary to von Weimarn's contention, Odén,[6] working with barium sulfate, showed the absence of a maximum in the concentration-size of particle curve, and demonstrated that the degree of dispersion always diminishes as the concentration of reacting ions increases. By

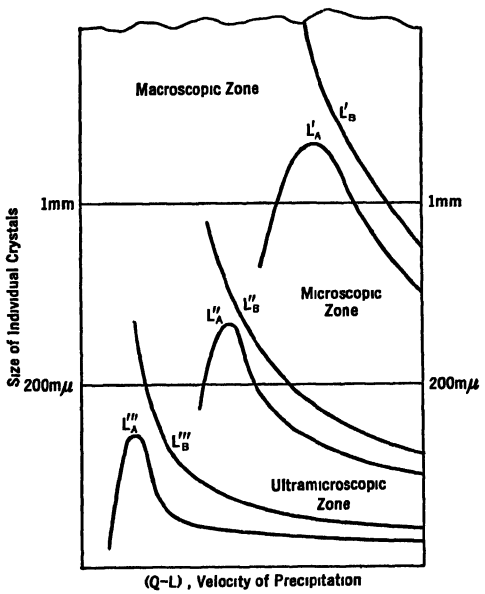


FIG. 1.—Schematic representation of von Weimarn's precipitation laws.

means of a special apparatus, Odén measured the distribution of various sizes of particles of barium sulfate thrown down on mixing varying concentrations of ammonium sulfate and barium thiocyanate. He found that aggregates of secondary particles are very often formed with quite small particles: above 100 mμ scarcely any are obtained, but below 20 mμ aggregates nearly always result if no special precautions are taken, such as the addition of citrate, to redisperse the

[6] Arkiv Kemi, Mineral. Geol, **7**, No. 26 (1920); Svedberg's "Formation of Colloids," London, 94 (1921).

aggregates. Odén attributed the difference between his observations and those of von Weimarn to the failure of the latter to recognize the existence of aggregates formed at certain concentrations, even though he was looking for them. Odén's results are in agreement with those for condensation in gases where the degree of dispersion increases regularly as the concentration rises (Vol. 1, p. 6). On the other hand, Bružs [7] obtained evidence of the existence of a region of maximum grain size of barium sulfate with certain concentrations of reagents, from measurements of the surface energy by a calorimetric method.

It should be pointed out that von Weimarn calls all precipitates crystalline but he believes liquids and gases to be crystalline, which suggests that he is not using the term in its ordinary sense. Even the most gelatinous precipitates of barium sulfate give the x-ray diffraction pattern of heavy spar,[8] and it is probable that most salt precipitates are crystalline to x-rays. At the same time, the author does not believe with von Weimarn that there is no such thing as an amorphous state in nature; but if one accepts von Weimarn's criterion that the amorphous state must be completely without vectoriality, it is probable that nothing completely amorphous exists.[9]

The Law of Corresponding States

The Simplified Expression; Limitations. Von Weimarn recognized that the velocity W of the first stage of precipitation cannot be measured in actual practice, and that, in many cases especially interesting in the synthesis of colloid systems, the velocity V of the growth of particles cannot be determined. In due time, therefore, he introduced a specific coefficient called the "precipitate form coefficient" or "dispersity coefficient" N, which is given by the expression:

$$N = \frac{P}{L} \cdot K_{ab} \cdot K_{cd} \cdot K_{bd} \cdot K_{ac} \cdot Z \qquad (4)$$

in which P/L is the percentage supersaturation, as in the velocity equation; Z, the viscosity; and K_{ab}, K_{cd}, etc., represent the "physical and chemical association" of the substances AB, CD, etc., which enter into the reaction AB (in solution) $+$ CD (in solution) $=$ AC (precipitate)

[7] J. Phys. Chem., **34**, 621 (1930); Bružs and Jankauskis: Chem. Abstracts, **24**, 4197 (1930).

[8] Von Weimarn and Hagiwara: Kolloid-Z., **38**, 129 (1926).

[9] Von Weimarn and Hagiwara: Japan J. Chem., **3**, 15 (1926); von Weimarn: Kolloid-Z., **44**, 279 (1928).

$+ AC$ (in solution) $+ BD$ (in solution). As a first approximation all factors except P/L may be neglected, that is,

$$N = \frac{P}{L} \tag{5}$$

or taking into account all factors in addition to P/L

$$N = J\frac{P}{L} \tag{6}$$

in which J has the same significance as in Equation (2).

Now if N is taken as approximately equal to P/L, then for the different substances x, y, and z,

$$N_x = \frac{P_x}{L_x}; \quad N_y = \frac{P_y}{L_y}; \quad \text{and} \quad N_z = \frac{P_z}{L_z}.$$

If the character of the precipitate is to be the same, irrespective of the chemical nature of the salt; in other words, if

$$N_x = N_y = N_z$$

then

$$\frac{P_x}{L_x} = \frac{P_y}{L_y} = \frac{P_z}{L_z} \tag{7}$$

This is the simplest expression for von Weimarn's law of corresponding states for the precipitation process, which says that, under corresponding conditions of precipitation, the mean magnitude (expressed in gram molecules) of the crystals of substances capable of precipitation will be the same. In the form given in Equation (7) the so-called law can hardly be regarded as a first approximation, even with substances that are related chemically. This is illustrated by the observations of Buchner and Kalff [10] for two series of related salts, as given in Table II. The solubility L is given in equivalents per liter, and N is calculated, for the concentrations (in equivalents) employed, from the expression $N = P/L$.

Considering the first group of salts, it will be seen that the nature of the precipitate is essentially the same although the values of N vary between 75 and 100,000. Von Weimarn observed the rapid formation of definite crystals of $BaSO_4$ at values of N varying between 50 and 20,000 (Table I). The law of corresponding states in its

[10] Rec. trav. chim., **39**, 135 (1920).

simplest form would require that, under the conditions recorded in Table II, calcium sulfate, calcium fluoride, and barium fluoride should give definite crystals instead of clear jellies. Turning to the silver halides, if von Weimarn's so-called law were applicable in its simplest form, these salts should give jellies more stable than barium sulfate under the conditions used; but instead, they give transparent drops

TABLE II

PHYSICAL STATES OF PRECIPITATES

Salt	L	N	State of precipitate
CaF_2	4×10^{-4}	3,400	Clear jelly, very stable
BaF_2	18×10^{-3}	75	Clear jelly, very stable
$CaSO_4$	3×10^{-2}	140	Clear jelly, stable
$BaSO_4$	2×10^{-5}	100,000	Clear jelly, stable
AgCl	1×10^{-5}	700,000	Jelly, very instable
AgBr	7×10^{-7}	8,000,000	Jelly, very instable
AgI	1.5×10^{-8}	300,000,000	Jelly, very instable
PbI_2	4.8×10^{-3}	360	Jelly, very instable

which cloud up and disintegrate in a few seconds into flocs of an entirely different physical character from the barium sulfate jelly. Finally, the small value of N for lead sulfate would lead one to expect the formation of a definitely crystalline precipitate; actually, a jelly results temporarily.

An even more striking exception to the simplified formulation is magnesium arsenate, which can be made to form a clear stiff jelly by mixing quite dilute solutions of potassium arsenate and manganese sulfate (p. 92). The value of L for the precipitate is so large that precipitation is slow and quantitative precipitation impossible in the dilute acid solution; hence $P/L = N$ is quite small.

Solubility and Crystal Size. It was observed by Hulett[11] and confirmed by Dundon[12] that the addition of finely ground calcium sulfate or barium sulfate to saturated solutions of their respective salts caused an increase in conductivity which rose to a maximum and then decreased slowly, finally approaching that of the normally saturated solution. This changing conductivity is usually attributed to changing

[11] Z. physik. Chem., **37**, 385 (1901).
[12] J. Am. Chem. Soc., **45**, 2658 (1923).

solubility with particle size. From measurements of particle size and of solubility, it is possible to calculate the surface tension. Dundon has done this for several substances using the equation of Dundon and Mack.[13] The results are given in Table III, in which M stands

TABLE III

Substance	M	ξ	$M.V.$	Diameter μ	Increase in solubility %	Temp °C	σ	Hardness
$BaSO_4$ (H)	233	4 5	52 0	0 1	80	25	1250	2 5–3 5
$BaSO_4$ (D) . ..	233	4 5	52 0	0 2	90	30	3000	2 5–3 5
$CaSO_4 \cdot 2H_2O$.	172	2 32	74 2	0 2–0 5	4.4–12	30	370	1 6–2
$SrSO_4$	184	3 96	46 4	0 25	26	30	1400	3.0–3 5
Ag_2CrO_4	332	5 52	60 1	0 3	10	26	575	2 (approx.)
PbI_2 . ..	461	6 16	74 8	0 4	2	30	130	Very soft
PbF_2	245	8 24	29 7	0 3	9	25	900	2 (approx.)
CaF_2 . ..	78	3 18	24 6	0.3	18	30	2500	4

for the molecular weight; ξ, the density of crystal; $M.V.$, the molecular volume; r, the radius of particle measured microscopically; and σ, the surface tension of particle.

Considering slightly soluble salts which are completely dissociated and whose activity coefficients may be taken as unity, the relation between increase in solubility on the one hand and size of crystals and surface tension on the other may be represented by the equation:

$$\frac{RT}{M} \ln \frac{S_r}{S} = \frac{2\sigma}{\xi r}$$

in which S_r is the solubility of particles with radius r; and S is the solubility of normal crystals.

By means of this equation and Dundon's data Kolthoff[14] calculated the ratio S_r/S for three salts at a size $r = 0.02$, obtaining the following: for $BaSO_4$, 930; for Ag_2CrO_4, 4.0; for PbI_2, 1.38. Assuming that Dundon's data give at least the order of magnitude of the surface tension of various crystals, it appears that the solubility

[13] J. Am. Chem. Soc, **45**, 2479 (1923); *cf.* Ostwald: Z. physik. Chem., **34**, 495 (1900); Freundlich: "Kapillarchemie," 144 (1909).

[14] J. Phys. Chem., **36**, 860 (1932).

of very small crystals of barium sulfate is about 1000 times greater than that of larger crystals, whereas the solubility of silver chromate increases only 4 times and that of lead iodide only 1.4 times under the same conditions.

Kolthoff points out how the differences noted above will explain the fact that substances of about the same solubility and precipitated under analogous conditions give entirely different forms of precipitates, contrary to von Weimarn's predictions. For example, silver chloride and barium sulfate have solubility products of about the same order of magnitude, but the former always comes down in flocs and the latter in the form of microcrystals under analytical conditions. This can be explained from the difference in solubility with crystal size for the two salts. Starting with such concentrations of the respective reacting ions that the macroscopic supersaturation of the salts are the same, one obtains soft crystals [15] of the silver chloride whose solubility is more or less independent of the crystal size and relatively hard crystals of barium sulfate whose solubility varies greatly with the crystal size. Since the solubility of the primary particles (nuclei) of silver halide first formed is about the same as that of large crystals and the solubility of the primary particles of barium sulfate is much larger than that of large crystals, it follows that the solution will be much less supersaturated with respect to the small particles of barium sulfate on the one hand than of silver chloride on the other. From Equations (2) and (3) we see that the velocity of formation of nuclei and growth on nuclei increases with increasing supersaturation; therefore the formation of nuclei is more spontaneous with the silver salt than with the barium salt. The rapid formation of so many nuclei of silver chloride soon exhausts the solution; under these conditions, little or no growth on nuclei takes place and the precipitate is a flocculent, colloidal mass. With barium sulfate, much fewer nuclei form under the same conditions; these grow at the cost of ions left in solution, and a microcrystalline mass results. Kolthoff [16] points out further that Böttger's [17] relation between the sensitivity, E, of a precipitation reaction and the solubility, L, of the particles: $E = L + V$, where V is the visibility of the particles, has no general validity. It will hold only if the "micro" and "macro" solubilities of the substance are approximately the same as those of the silver halides.

[15] *Cf.* Reis and Zimmermann: Z. physik. Chem., **102**, 299 (1922).

[16] Z. anal. Chem. Böttger Festschrift, **86**, 34 (1931).

[17] Chem.-Ztg., **33**, 1003 (1909); **36**, 1097 (1912); Z. angew. Chem., **25**, 1992 (1912); Gorski: Z. anorg. Chem., **81**, 315 (1913).

In this connection Balarew [18] questions whether the changing conductivity (p. 19) on adding finely ground barium sulfate, say, to the saturated solution of the salt is due primarily to varying solubility with particle size. Balarew attributes the initial increase in conductivity to (1) the presence of barium chloride in the sulfate, (2) the greater solubility of broken than of complete crystals, and (3) the breaking up of atomic aggregates. The subsequent fall in conductivity could be caused partly by the crystallizing out of barium sulfate on account of the solution of the chloride; but the velocity of crystallization is much greater than the rate of fall of conductivity so that the latter is attributed to the slow restoration of equilibrium between the complete and broken crystals. Although the greater solubility of broken crystals may be the determining factor in the experiment referred to, there is no doubt that, below a certain size, the solution pressure of smaller particles is greater than that of larger ones. Balarew raises but does not settle the question as to whether Hulett's experimental method gives a true measure of the change in solubility with crystal size.

The Generalized Expression; Applicability and Limitations. Von Weimarn's [19] explanation of the above discrepancies is, of course, that the law of corresponding states for the precipitation process is not the simple expression:

$$\frac{P_x}{L_x} = \frac{P_y}{L_y} = \frac{P_z}{L_z} \cdots$$

but

$$J_x \cdot \frac{P_x}{L_x} = J_y \cdot \frac{P_y}{L_y} = J_z \cdot \frac{P_z}{L_z} \cdots$$

in which J_x, J_y, and J_z are specific variable multipliers, the value for any substance being "the product of all other factors (in addition to P/L) which influence the crystallization process. These values must be expressed by abstract numbers such that the values for P/L are equivalent." [19] In other words, von Weimarn's equation for his so-called law becomes quantitative and generally applicable by introducing "variable multipliers," handy wastebaskets, as it were, into which are thrown all the variable factors known or unknown which have not been evaluated. Von Weimarn also calls attention to the fact

[18] Z. anorg. Chem., **145**, 122 (1925); **151**, 68; **154**, 170 (1926); **163**, 213 (1927); Kolloid-Beihefte, **30**, 249 (1930); **32**, 205; *cf* Stranski: 197 (1931).

[19] Kolloid-Beihefte, **18**, 48 (1923).

that the L-value employed in the calculation should not be the known solubility in the pure solvent but some other value which corrects for the effect of electrolytes in the surrounding solution.[20]

Although it is possible to express facts fairly accurately by means of such flexible formulas, it is doubtful whether anything is gained scientifically by regarding formulations of this kind as quantitative representations of natural laws. Von Weimarn evidently thinks so, but his opinion is not shared generally. Bancroft[21] prefers to discard the formulas altogether and state the whole thing from another point of view. He points out that the mean size of the crystals is determined by the total amount of material crystallizing and the number of nuclei. The really important thing, therefore, is the number of nuclei which are formed under any given conditions. It is contended, very properly, that factors other than percentage supersaturation influence the number of nuclei formed. Thus the specific nature of the substance, stirring, and temperature have a profound effect on nuclei formation, and adsorption exerts a marked influence on the growth of particles.[22,23] Freundlich[24] likewise does not believe that the separation of a solid phase is generally and uniformly regulated by its solubility and the supersaturation prevailing: "At the same degree of supersaturation, the velocity of formation of nuclei, the velocity of crystallization, and the ratio between the two are quite different for different substances; and they may be influenced in very different ways by foreign substances, perhaps by the ions present during precipitation."

Every analytical chemist is aware of the marked effect on the physical character of precipitates of the presence of foreign ions in solution. Barium sulfate comes down in a more finely divided state when precipitated with sulfate in excess than when precipitated with barium in excess.[25] Since, in general, any substance which is adsorbed by a second will tend to peptize the latter, it follows that, other conditions being the same, barium sulfate will come down most finely divided when precipitated in the presence of those substances which it adsorbs most strongly.[22] Now barium sulfate adsorbs its own ions

[20] Von Weimarn: Kolloid-Z., **2**, 278 (1908); **32**, 145 (1923).
[21] J. Phys. Chem., **24**, 100 (1920).
[22] Weiser: J. Phys. Chem., **21**, 314 (1917).
[23] *Cf.* von Weimarn: "Grundzuge der Dispersoid Chemie," 97 (1911).
[24] "Kapillarchemie," 3rd ed., **2**, 78 (1932).
[25] Foulk: J. Am. Chem. Soc., **18**, 803 (1896); *cf.* Popoff: Ind. Eng. Chem., Anal. Ed., **2**, 230 (1930).

strongly, and hydrogen ions are adsorbed more strongly than most cations; accordingly, when sulfuric acid is treated with barium chloride in excess, the precipitate tends to come down in a finely divided state. This effect is sufficiently great to peptize the salt as a positive sol under suitable conditions. The precipitate would come down in a very finely divided form in the presence of a slight excess of sulfuric acid, in which it is less soluble than in water,[26] were it not that the strongly adsorbed hydrogen ion counteracts the effect of the adsorbed sulfate. With potassium sulfate in excess the precipitate is finer than with sulfuric acid in excess, since potassium ion is not strongly adsorbed. As would be expected, the presence of hydrochloric acid tends to give a coarser precipitate because of the solvent action of the acid.

Von Weimarn's reply is that all the several specific factors other than P/L are taken into account by means of the variable multiplier. It seems rather unfortunate that von Weimarn attributed the criticism of his point of view to misunderstanding owing to incomplete knowledge of his work. It is more likely that people understand it too well and so refuse to recognize the general validity of a so-called law which is formulated by the use of a variable multiplier made up of an indefinite number of unevaluated factors.

Although the separation of a solid phase is not regulated generally and uniformly by its solubility and the prevailing supersaturation, it should be especially emphasized that certain statements of von Weimarn have quite general validity. Thus, when the reacting solutes are very dilute, the resulting solid precipitates in a definitely crystalline form. At low concentrations, the velocity of formation of nuclei is small and the few nuclei which do form grow so slowly at the cost of the solute present in weakly supersaturated solution that large crystals result. Conversely, when the reacting solutions are very concentrated, jellies are formed consisting of drops of the liquid surrounded by the solid. The rate of formation of nuclei is extremely high at the high concentration, so that at any point where the two solutions touch there is formed immediately a feltwork of nuclei which do not have time to crystallize further, and so yield a solid film. Subsequently, the nuclei grow into crystals as the interacting substances diffuse through the film.[27]

In contradistinction to von Weimarn's views, Haber[28] is of the

[26] Hammett and Deyrup: J Am. Chem. Soc, **55**, 1900 (1933).
[27] *Cf.* Freundlich: "Kapillarchemie," 2nd ed., 632 (1922).
[28] Ber., **55B**, 1717 (1922).

opinion that the form of precipitates is influenced primarily by the following two factors: aggregation velocity and orientation velocity. When the limit of solubility is exceeded for a given substance, the molecules or molecular aggregates tend to group together into larger aggregates. The velocity of this process is a function of the supersaturation; hence, the higher the supersaturation, the less regular will be the aggregates. The absolute concentration of the reacting ions will also be of importance. By mixing the molecules in a more or less arbitrary manner, instable aggregates are formed which lose energy and become oriented in a regular way in the crystal lattice. The speed of this process is termed the orientation velocity. From Haber's point of view the form of a given precipitate depends upon its relative velocity of orientation and of aggregation: if the supersaturation is very high, the aggregation velocity will predominate and the resulting precipitate will be amorphous to x-rays; whereas, if the supersaturation is sufficiently low, the orientation velocity predominates and the precipitate is crystalline. A precipitate, amorphous to x-rays, becomes crystalline during the aging process. Since the orientation velocity varies with different substances, it follows that, at the same degree of supersaturation, the form of a precipitate will vary with different substances.

The Analytical Precipitate

As noted above, barium sulfate comes down in a less finely divided, more readily filterable form when precipitated with excess sulfate. But since the analyst is usually called upon to determine sulfate rather than barium, the question of getting the precipitate in the proper form for quantitative filtration has received considerable attention. A readily filterable precipitate is ordinarily obtained by adding the barium salt drop by drop with vigorous stirring to the boiling sulfate solution containing a small amount of hydrochloric acid. Since the solubility of barium sulfate is increased greatly by the presence of acid, the concentration of the acid is ordinarily kept quite low. Murmann [29] points out that complete precipitation results in the presence of a relatively large amount of hydrochloric acid provided ethyl alcohol is added and the filtration carried out in the cold.

Although slow addition of barium chloride to the hot sulfate solution acidified slightly with hydrochloric acid ordinarily yields a granular, readily filterable salt, an occasional precipitate is obtained which

[29] Oesterr. Chem.-Ztg., **13**, 227 (1911).

is too fine to be retained, even by a close filter. It is common practice to digest such a precipitate at the boiling point until it takes on the desired physical character. The coalescence of barium sulfate precipitates by digestion is ordinarily attributed to the growth of larger particles at the expense of smaller ones, but Trimble [30] showed that the solution pressure of barium sulfate at about 100° ceases to be a function of particle size for particles larger than about 2μ in diameter. Odén [31] boiled a suspension of barium sulfate for 100 hours and observed that the number of particles under 0.2μ in radius was decreased only from 47% to 30%. The observed coalescence by digestion in the mother liquor is apparently caused by the collection of the particles into relatively larger clumps, followed by the cementing together of the unit particles into aggregates which are retained by the filter. Balarew [32] believes that the setting up of equilibrium in a suspension of finely ground crystals of a difficultly soluble salt involves two kinds of processes: molecular and submicronic solution together with peptization and molecular and submicronic growth. Kolthoff [33] finds that Ostwald ripening is of subordinate significance in the aging of precipitates at room temperature. Aging in the mother liquor consists in the perfection of very imperfect crystals as a result of recrystallization without always being accompanied by pronounced changes of the external surface. It was found that all factors which decrease the solubility of the precipitate inhibit the speed of the perfecting process; and all factors which increase the solubility promote recrystallization and the perfecting process. It was concluded that the recrystallization takes place in a liquid film around the primary particles and hence that the speed of perfection is determined by the solubility in the liquid film rather than the solubility in the bulk of the solution. To speed up the growth of larger particles at the expense of smaller ones, Krak [34] recommends pouring off the supernatant liquid and adding 10 cc of saturated ammonium acetate, the solvent action of which causes the particles to grow to readily filterable dimensions.[35]

[30] J. Phys. Chem., **31**, 601 (1927).

[31] Svensk Kem. Tid, **32**, 74, 90, 108 (1920); Chem. Abstracts, **15**, 971 (1921).

[32] Kolloid-Z., **66**, 51 (1934); Z. physik. Chem., **B28**, 78 (1935).

[33] Science, **84**, 376 (1936); Kolthoff and Noponen: J. Am Chem Soc, **59**, 1237 (1937).

[34] Chemist-Analyst, **5**, 26 (1912).

[35] Osborne: J. Phys. Chem., **17**, 629 (1913).

Adsorption by Precipitated Barium Sulfate

Historical

Because of the intrinsic importance of barium sulfate in quantitative analysis, its adsorptive power has been the subject of numerous investigations. A quantitative study of the contamination of the precipitate formed by the addition of sulfuric acid to barium chloride and the reverse was first carried out by Richards and Parker[36] and by Hulett and Duschak.[37] The latter observed that barium chloride is taken up not only during precipitation but also when finely divided crystals are suspended in a solution of the salt. To explain the phenomenon, they consider the possible formation of complex salts such as $BaClHSO_4$ and $(BaCl)_2SO_4$.[38] Schneider[39] investigated quantitatively the contamination of barium sulfate by ferrous sulfate, and Creighton[40] made a similar study of the contamination with aluminum sulfate. Both Schneider and Creighton regard the phenomenon as an example of solid solution, whereas Richards[41] compared the contamination with ferric sulfate to the occlusion of hydrogen by palladium which involves both compound formation and adsorption (Vol. I, p. 218). The work of Küster and Thiel[42] and of Korte,[43] who repeated and extended Schneider's experiments, indicates, however, that the contamination is an adsorption phenomenon. Indeed, an adsorption mechanism of some sort seems to offer the only plausible explanation of the fact that barium sulfate carries down all manner of substances from either true[44] or colloidal[45] solutions; and most investigators accept this explanation.[46] Thus from precise observa-

[36] Z. anorg Chem., **8**, 413 (1895).

[37] Z anorg Chem., **40**, 196 (1904).

[38] *Cf.* Folin: J. Biol. Chem., **1**, 131 (1906); Karaoglanow: Z. anal. Chem. **106**, 129 (1936).

[39] Z. physik. Chem., **10**, 425 (1892); Glendinning and Edgar: Chem. News, **24**, 140 (1871); Sloane: **44**, 221 (1881); Jannasch and Richards: J. Prakt Chem., (2) **39**, 321 (1889).

[40] Z. anorg Chem., **63**, 53 (1909).

[41] B. anorg. Chem., **23**, 383 (1900)

[42] Z. anorg. Chem., **19**, 97 (1899); **22**, 424 (1900)

[43] J Chem. Soc, **87**, 1503 (1905).

[44] Patten: J. Am. Chem. Soc, **25**, 186 (1903).

[45] Vanino and Hartl: Ber., **37**, 3620 (1904).

[46] Wohlers· Z. anorg Chem., **59**, 203 (1908); Allen and Johnston· J. Am Chem. Soc., **32**, 588 (1910); Johnston and Adams: **33**, 829 (1911); Weiser: J. Phys. Chem., **21**, 317 (1917); Koelsch: Chem-Ztg., **43**, 117 (1919); Odén: Arkiv Kemi, Mineral. Geol., **7**, No. 26, p 92 (1920); Dhar, Sen, and Chatterji: Kolloid-Z., **33**, 29 (1923); *cf., however,* Smith: J. Am. Chem. Soc., **39**, 1152 (1917); Kolthoff and Vogelenzang: Z. anal. Chem., **58**, 49 (1919).

tions on the carrying down of a large number of cations by barium sulfate Johnston and Adams[47] conclude "that this occlusion is a phenomenon of adsorption at the surface of the grains of the precipitate and that its amount depends upon (*a*) the composition of the original solution, (*b*) the initial fineness of the precipitate, and (*c*) the amount of recrystallization which has taken place." Although most people subscribe to this general point of view there is a difference of opinion as to the exact nature of the adsorption process and the factors which influence it. The several mechanisms will be considered in the subsequent paragraphs.

Adsorption of Cations

Adsorption of Cations of the Commoner Elements. The first systematic study of the adsorption by barium sulfate of a series of common cations was made by Johnston and Adams. In Table IV are given the amounts of the several cations (expressed as the sulfate) adsorbed by 1 g of $BaSO_4$ thrown down in the hot with a slight excess of barium chloride from solutions 0.003 *N* in HCl and containing the metallic chlorides in the initial concentration $A = 0$ and

TABLE IV

ADSORPTION OF CATIONS BY BARIUM SULFATE

Metal	Sulfate adsorbed by 1 g of $BaSO_4$			
	A		*B*	
	Millicquivalent	Millimol	Millicquivalent	Millimol
Mg	0 048	0 024		
Li	0 033	0 033	0 040	0 040
Na	0.029	0 029	0 043	0 043
K	0 033	0 033	0 035	0 035
Al	0 051	0 017	0 060	0 020
Fe (ous)	0 074	0 037	0 120	0 060
Ni	0 062	0 031	0 100	0 050
Cu	0 082	0 041	0 100	0 050
Zn	0 080	0 040	0 100	0 050
Mn	0 128	0 064	0 160	0 080
Cd	0 160	0 080	0 180	0 090

[47] J. Am. Chem. Soc., **33**, 829 (1911).

$B = 0.1N$. The time of precipitation was 4 minutes, and the time of standing 18 hours. The adsorption values obtained under these conditions are of the same order of magnitude; nevertheless, they show considerable variation. If the values are expressed in equivalents, one can detect the tendency for ions of higher valence to be more strongly adsorbed in accord with Schulze's rule. This tendency is less marked when the adsorption values are expressed in mols. Moreover, when so expressed, the adsorption of trivalent aluminum is less than that of either the univalent or bivalent ions. In this respect aluminum appears quite different from trivalent lanthanum which Frion[48] found to be adsorbed much more strongly than bivalent magnesium.

Observations of adsorption on barium sulfate by Paneth[49,50] and on the silver halides by Fajans[51] led to the conclusion that those ions will be most strongly adsorbed by a heteropolar adsorbent whose compounds with the oppositely charged ions of the ion lattice are least soluble. This is known as Paneth-Fajans' rule. According to this rule the adsorption should be in the order: Cu > Ni > Mg > Cd > Mn > Zn; but the order actually obtained by Johnston and Adams is quite different, as follows: Cd > Mn > Zn, Cu > Ni > Mg > Al.

Although recognizing the applicability of Paneth-Fajans' rule under certain conditions, Težak[52] suggests that in the case at hand the adsorbability should increase with the similarity of the constitution of the ions with one of the ions of the adsorbing lattice. Now barium ion is very strongly adsorbed by barium sulfate, and it has the same electron structure as xenon. Magnesium, on the other hand, is the most weakly adsorbed of the bivalent cations, and it has the configuration of neon. Since the adsorbability falls off in the series: xenon, krypton, argon, neon, it is deduced that the order of adsorption of the bivalent cations should be: Ba > Hg > Pb > Cd > Mn > Zn > Cu > Ni > Mg in agreement with the above-mentioned observations of Johnston and Adams. From the peptizing action on secondary aggregates of barium sulfate, Težak[53] deduces the order of adsorption for two series of ions to be: Cd > Mn > Cu > Ni >

[48] J. chim. phys., **7**, 101 (1909).
[49] Physik. Z, **15**, 924 (1914)
[50] Horovitz and Paneth: Z. physik. Chem., **89**, 513 (1915).
[51] Fajans and Beckerath: Z physik Chem., **97**, 478 (1921)
[52] Kolloid-Z, **59**, 158 (1932).
[53] Z physik. Chem., **A175**, 284; **B32**, 46, 52 (1936).

Zn > Mg; and K > Na > Li, which is the reverse of the order of the hydration of the ions in the two series.

The coprecipitation of ferrous sulfate with barium sulfate was attributed by Giacalone and Russo [54] to both occlusion and adsorption occurring simultaneously. It was found that the contamination at varying concentrations may be expressed by Freundlich's adsorption equation. Coprecipitation was prevented entirely by adding ammonium thiocyanate to the solution having 1% or less of ferric chloride and warming to the point of decoloration, *i.e.*, complete reduction, before precipitating the barium with sulfuric acid.

Pincus and de Brouckère [55] have made extensive investigations of the adsorption of a number of metallic halides by barium sulfate which was precipitated, washed, kept in alcohol to prevent growth of crystals, and finally dried at 100° before use. The star-shaped aggregates below 10^{-5} cm in diameter were made up of ultramicroscopic granules. The results of the adsorption studies indicate that the anion and cation of the salts are adsorbed in equivalent amounts and that the adsorption is reversible, the same equilibrium value being obtained from both sides. Some typical adsorption curves are shown in Fig. 2, in which the log of the adsorption, x, in mols per gram of adsorbent is plotted against the equilibrium concentration. It will be seen that all the isotherms consist of two rectilinear parts connected by a smooth curve. In every isotherm the first part is an approximately straight line which makes an angle of about 45° with the axes, indicating that in sufficiently dilute solutions the adsorption is nearly proportional to the electrolyte concentration. The second part of the curve, which runs parallel to the abscissa axis, corresponds to saturation of the surface. This course of the isotherm is explained by assuming that a more or less discontinuous monomolecular adsorption layer is formed. From this point of view the maximum amount that can be fixed on a given surface would depend chiefly on the diameters of the adsorbed particles, as the results seem to indicate. The amount of electrolyte adsorbed on a positively charged surface appears to depend more on the nature of the anion than on that of the cation; thus the valence of the cation plays no marked rôle in the adsorption. De Brouckère explains this by assuming that the anions are adsorbed directly to the barium sulfate surface and an equivalent amount of cations are held

[54] Gazz. chim. ital., **66**, 631 (1936).

[55] J. chim. phys., **25**, 605 (1928); de Brouckère: **26**, 250 (1929); **27**, 543 (1930); Bull. soc. chim Belg, **39**, 174 (1930); **45**, 353 (1936); Ann. chim., **19**, 79 (1933).

by electrostatic attraction. On the other hand, with negatively charged particles the cations are in contact with the surface. Experiments carried out with lead and thallium halides show that the quantity adsorbed is greater the less the solubility, in accord with Paneth-Fajans' rule. Complex ions such as found in mercury and cadmium halides and the I_3 anion are adsorbed to a larger extent than simple ions. The adsorption of iron is 10 to 200 times stronger than the cations of univalent and bivalent salts, which are not readily hydro-

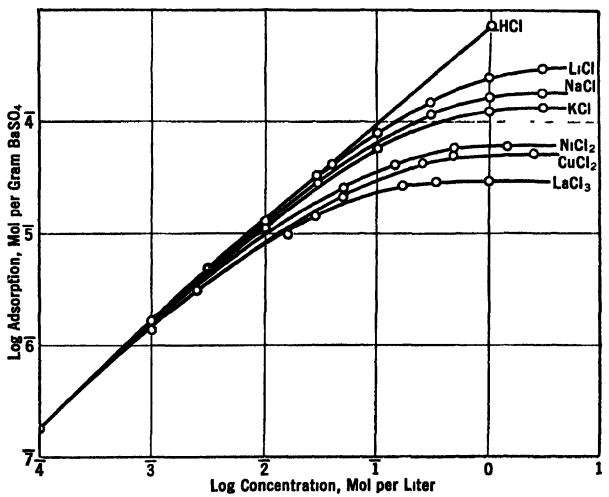


FIG 2.—Adsorption of metallic halides by barium sulfate.

lyzed, not because of the trivalence of the iron but because the iron in ferric chloride solutions is in the form of colloidal micelles which are strongly and irreversibly adsorbed.[56]

The solvent is adsorbed to some extent by barium sulfate (p. 14), but the ratio KCl/H_2O was found to be greater in the adsorption film than in the solution.[57]

Balarew and Koluschewa[58] claim that the adsorption mechanism is not so simple as assumed by Težak and de Brouckère. Thus the

[56] De Brouckère: Bull. sci. acad. roy. Belg, **13**, 827 (1928); Bull. soc. chim. Belg., **38**, 409 (1929).

[57] De Brouckère: Bull soc. chim. Belg., **41**, 412 (1932); *cf.* Dumanskii: Kolloid-Z., **65**, 178 (1933).

[58] Kolloid-Z., **67**, 203 (1934).

order of cation adsorption is for the most part the reverse of that deduced by Težak provided the barium sulfate is precipitated in the presence of a large excess of sulfate. Balarew [59] believes that most of the adsorption is on the internal surface of the crystals and only a relatively small part on the outermost part of the crystals. He points out that, in a suspension of barium sulfate in potassium chloride solution, the following equilibrium is set up: $2KCl + BaSO_4 \rightleftarrows BaCl_2 + K_2SO_4$. He concludes that potassium chloride is not adsorbed directly on the barium sulfate surface; on the contrary, the sulfate ions are believed to constitute the inner portion of the adsorption layer with the chloride ions farther from the surface. In support of this he [60] claims that a precipitate thrown down in an almost saturated solution of potassium chloride and containing 6.25% K_2SO_4 and 3.11% H_2O is free from adsorbed chloride. He believes that the adsorption of cations follows Paneth-Fajans' rule in a given group of the periodic system and that the adsorption of simple inorganic anions follows the Hofmeister series.

Kolthoff [61] likewise criticizes de Brouckère's work on both experimental and theoretical grounds. Kolthoff, like Balarew, believes that most of the adsorption by crystalline precipitates takes place in the fine cracks and capillaries which constitute the inner surface. It is believed that in the first stage of the process the adsorbed ion displaces ions in the surface layer of the adsorbent. For the adsorption of lead ion, say, the distribution coefficient K is given by the expression:

$$\frac{\text{Pb (surface)}}{\text{Pb (solution)}} = K \frac{\text{Ba (surface)}}{\text{Ba (solution)}}$$

Other factors which may enter into the process are: true adsorption at active centers only; true adsorption followed by secondary precipitation of the displaced lattice ion; exchange with a third kind of ion already adsorbed on the precipitate; molecular adsorption; and activated adsorption in which the adsorbed substance may be ionized on the surface. Kolthoff's views will be taken up in some detail in the next chapter. The differences in the experimental results of

[59] Z. anal. Chem., **72**, 303 (1927); Kolloid-Beihefte, **30**, 249 (1930); **32**, 304; **33**, 310 (1931).

[60] Balarew: Kolloid-Beihefte, **30**, 281 (1930).

[61] Chem. Weekblad, **31**, 230, 244, 251 (1934); Kolthoff and Noponen: J. Am. Chem. Soc., **59**, 1237 (1937); *cf. reply by* Pinkus: Bull. soc. chim. Belg., **44**, 637; de Brouckère: 625 (1935).

de Brouckère and Kolthoff are due in part at least to differences in the nature of the adsorbent and variations in the experimental procedure.[62] The differences can be reconciled, if at all, only by each investigator working with samples of adsorbent prepared by the other.[63]

Adsorption of Radium and Radioactive Cations. Germann[64] first investigated the adsorption of radium by barium sulfate and showed that the same laws which apply to the adsorption of ponderable masses are applicable with an equal degree of accuracy to masses as small as 5×10^{-8} g adsorbed per gram of adsorbent. The observations were made by adding a known amount of radium-free barium sulfate to 80 cc of a standard solution of radium barium chloride, which was allowed to stand until adsorption equilibrium was established, after which the barium sulfate was filtered off and the supernatant liquid analyzed for the radium content by the emanation method. The data are reproduced in Table V. These data are in accord with Freund-

TABLE V

ADSORPTION OF RADIUM BY BARIUM SULFATE

$BaSO_4$ employed $= m$ g	Equilibrium concentration of Ra after adsorption $= c$ g/cc $\times 10^{10}$	Decrease in Ra concentration due to adsorption $= x$ g/cc $\times 10^{10}$
0 0	22 79	0 00
0 05	18 55	4 24
0 10	15 12	7 67
0 20	9 47	13 32
0 30	5 86	16 93
0 40	3 97	18 82
0 50	2 70	20 09

lich's adsorption formula $x/m = ac^{1/n}$, where x is the amount adsorbed by mass m of adsorbent, c the equilibrium concentration, and a and n constants, as evidenced by the fact that a straight line is obtained by plotting log x/m against log c.

In addition to radium, the active substance adsorbed by barium sulfate, when it is precipitated in solutions containing the radioactive

[62] De Brouckère: Bull. soc. chim. Belg, **45**, 279 (1936).
[63] *Cf.* Kolthoff: Bull. soc. chim. Belg., **45**, 270 (1936).
[64] J. Am. Chem. Soc., **43**, 1615 (1921).

constituents of uranium ores, is chiefly ionium,[65] accompanied by a relatively small amount of actinium, and not actinium alone as claimed by Debierne.[66] Strong adsorption of ionium by barium sulfate is indicated by the fact that the salt has a very great capacity for adsorbing thorium,[67] the isotope of ionium.

Paneth [49] and Horovitz [50,68] observed that radium is strongly adsorbed by barium sulfate and chromate whereas it is not adsorbed at all by hydrous chromic oxide and silver chloride. Since radium sulfate and chromate are soluble whereas radium oxide and chloride are not, Paneth was led to formulate what has come to be called Paneth-Fajans' rule (p. 103).

More recently Imre [69] has studied the velocity of adsorption of actinium, thorium B, radioactive lead, and radium on barium sulfate,

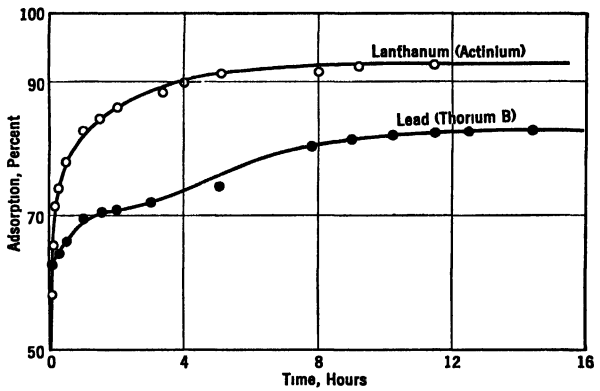


FIG. 3.—Velocity of adsorption of actinium and thorium B by barium sulfate.

confirming the observation of Paneth [50,68] that adsorption equilibrium is established only after a considerable time.[70] This is illustrated in Fig. 3. Although lead sulfate is less soluble than actinium sulfate, lead ion is adsorbed less strongly than actinium ion which is not in accord with Paneth-Fajans' rule; instead the ion of higher valence is the more strongly adsorbed, in accord with Schulze's rule.

[65] Kammer and Silverman: J. Am. Chem. Soc., **47**, 2514 (1925).
[66] Compt rend., **129**, 593 (1899); **130**, 906 (1900).
[67] Balcar and Stegemann: J. Phys. Chem., **32**, 1411 (1928).
[68] Paneth and Vorwerk: Z. physik. Chem., **101**, 445 (1922).
[69] Z. physik. Chem., **A153**, 262 (1931); **A164**, 327, 343, 364 (1933); **A171**, 239 (1934); Z. Elektrochem., **38**, 539 (1932).
[70] *Cf.* Kolthoff and Rosenblum: J. Am. Chem. Soc., **58**, 116 (1936).

The adsorption from a lead nitrate solution is believed by Imre [71] to take place in two stages: in the first, the surface of the barium sulfate lattice is covered with a layer of adsorbed lead nitrate; and in the second, the adsorbed ion is embodied in the solid surface layer. Kolthoff and MacNevin,[72] on the other hand, found that lead nitrate is not appreciably adsorbed by aged barium sulfate and that the measured adsorption of lead (ThB) is the result of an exchange between barium ions in the surface of the adsorbent and lead ions:

$$\underset{\text{Surface}}{BaSO_4} + \underset{\text{Solution}}{Pb^{++}} \rightarrow \underset{\text{Surface}}{PbSO_4} + \underset{\text{Solution}}{Ba^{++}}$$

virtually no nitrate ions being carried down (*cf.*, however, p. 37).

By making certain assumptions, Imre derived the expression for the coefficient of distribution, K, of ions between the adsorption surface and the solution, which for lead ion on barium sulfate is: $K = e^{(E_{Pb}-E_{Ba})/RT}$, in which E_{Pb} and E_{Ba} are the adsorption energy of lead ions and barium ions, respectively, on barium sulfate. The adsorption energy E is calculated from the expression $E = -L/N$, in which L is the heat of solution of the salt and N the number of ions in it. On such theoretical grounds, Imre calculated the value of K to be 0.64 at 20°. From his experimental work on the change of adsorption with temperature, of lead (ThB) on barium sulfate, Imre calculated a value of $K = 0.21$—0.39. Kolthoff and MacNevin made direct measurements of the distribution of lead sulfate between water and barium sulfate on small but well-aged crystals and found the value of $K = e^{(E_{Pb}-E_{Ba})/RT} = 0.12$; and for the distribution between 50% ethyl alcohol and barium sulfate, $K = 0.067$. Kolthoff believes that the first step in the adsorption consists of a rapid exchange between lead and barium ions in the surface of the adsorbent, followed by a slow incorporation of the exchanged lead in the barium sulfate lattice as a result of recrystallization. The lead adsorbed as a result of the kinetic exchange is readily displaced by surrounding the crystals with a large excess of barium salt. Although Kolthoff's views are different in some respects from those of Imre, it would appear that the general concept of both is similar in essential respects.[73]

Kolthoff [74] found that the surface of aged precipitates may be de-

[71] Z. physik. Chem., **A171**, 239 (1934).

[72] J. Am. Chem. Soc., **58**, 499, 725 (1936).

[73] *Cf.* Imre: Z. physik. Chem., **A177**, 409 (1936).

[74] Kolthoff: Chem. Weekblad, **31**, 395 (1934); *cf.* Kolthoff and MacNevin: J. Am. Chem. Soc., **58**, 725 (1936).

termined from adsorption of chemically identical ions. In such cases the total amount adsorbed on the surface equals that which has entered the lattice. This equality holds for ThB++ on lead sulfate but does not hold for ThB++ or Ra++ on barium sulfate where the adsorption is about double that in the crystal. The adsorption of radioactive ions can therefore be applied to calculate the specific surface only for isotopic ions; hence the expression of Paneth and Thimann [75] is not generally applicable (p. 50).

Adsorption of Anions

When an alkali is precipitated with barium chloride in slight excess, the most usual analytical procedure, the determinations are too low, since some sulfate is weighed as alkali sulfate and calculated as if it were pure barium sulfate.[76] Opposed to this is the adsorption of chloride probably as barium chloride, which tends to make the analytical results too high. The latter effect manifests itself especially in the precipitation of sulfuric acid by barium chloride and the reverse. Hulett and Duschak [37,77] found it possible to obtain exact results in such determinations by estimating the chlorine content of the precipitate and deducting the barium chloride equivalent from the weight of the crude barium sulfate. Although the adsorption of chloride ion by barium sulfate is appreciable, Mendelejeff [78] long ago showed it to be small compared to that of nitrate. It is therefore somewhat surprising that Kolthoff failed to observe any adsorption of nitrate from a lead nitrate solution. Mendelejeff's observation was confirmed in the author's laboratory [79] in the course of an investigation of adsorption of various ions by barium sulfate formed on mixing sodium sulfate with a definite excess of the barium salts of the respective ions. The extent of the adsorption was determined by direct analysis of the washed precipitate. In Table VI the ions are arranged in the order of equivalent adsorption, beginning with the most strongly adsorbed ferrocyanide. The adsorption in mols and the solubility of the

[75] Ber, **57B**, 1215 (1924).

[76] *Cf.* Hahn and Keim: Z. anorg. Chem., **206**, 398 (1932).

[77] *Cf.* Karaoglanow: Z. anal. Chem., **57**, 77 (1918).

[78] Pogg. Ann., **55**, 214 (1842).

[79] Weiser and Sherrick: J. Phys Chem, **23**, 205 (1919); *cf* Ghosh and Dhar: Kolloid-Z., **35**, 144 (1924); Chakravarti and Dhar: **44**, 63; **45**, 12 (1928); von Weimarn: Repts. Imp. Ind. Research Inst., Osaka, Japan, **12**, 153 (1931); Balarew, Koluschewa, and Totewa: Kolloid-Beihefte, **33**, 299 (1932); Chao, Hsiung, and Chu: J. Chinese Chem. Soc, **3**, 325 (1935); Schneider and Rieman, III: J. Am. Chem. Soc., **59**, 354 (1937).

several barium salts are also included in the table. From a consideration of the absolute amount of the adsorption in each case, there is little to suggest Schulze's rule; for, although a tetravalent ion appears to be adsorbed most strongly, four univalent ions are more strongly adsorbed than trivalent ferricyanide. Furthermore, contrary to what is implied in Schulze's rule, there is a wide variation in the amount of univalent ions adsorbed, nitrate being carried down 150 times more strongly than iodide (*cf.* p. 42).

TABLE VI

ADSORPTION OF ANIONS BY BARIUM SULFATE

Anion	Ion in excess	Adsorption by 100 mols $BaSO_4$		Solubility of barium salts, millimols per gram water at 25°
		Gram equivalents	Gram mols	
Ferrocyanide	Ba^{++}	13 20	3 30	0 07
Nitrate	Ba^{++}	8 48	8 48	0 40
Nitrite	Ba^{++}	7 47	7 47	3 10
Chlorate	Ba^{++}	5 84	5 84	1 25
Permanganate	Ba^{++}	2 85	2 85	1 93
Ferricyanide	Ba^{++}	2 70	0 90	Very soluble
Chloride	Ba^{++}	1 76	1 76	1 78
Bromide	Ba^{++}	0 83	0 83	3 57
Cyanide	Ba^{++}	0 31	0 31	4 25
Sulfocyanate	Ba^{++}	0 22	0 22	6 13
Iodide	Ba^{++}	0 06	0 06	5 43
Chloride	SO_4^{--}	0 125	0 125	1 78
Chlorate	SO_4^{--}	0 227	0 227	1 25
Permanganate	SO_4^{--}	0 137	0 137	1 93

Considering the relationship between the solubility of the several barium salts and the adsorbability of the respective anions by barium sulfate, one can note a tendency for the anions of the less soluble salts to be more strongly adsorbed, in accord with Paneth-Fajans' rule. There are, however, numerous exceptions to this qualitative statement. Thus nitrate ions are adsorbed to approximately the same extent as nitrite ions although they are but one-eighth as soluble. Kolthoff and MacNevin [80] determined the adsorption by barium sul-

[80] J. Am. Chem. Soc., **58**, 1543 (1936).

fate of a number of univalent anions from 50% ethyl alcohol. The results are given in Table VII. The adsorption follows the Freund-

TABLE VII

SOLUBILITY AND ADSORBABILITY

Barium salt	Order of adsorbability $a \times 10^4$	Relative solubility in 50% ethyl alcohol	Order of increasing solubility
Bromate	1 80	1	1
Formate	0 91	81	3
Nitrate	0 69	33	2
Perchlorate	0 59	1610	7
Chloride	0 54	223	4
Bromide	0 37	843	5
Iodide	0 35	1477	6
Thiocyanate	0 26	1663	8

lich adsorption isotherm, $x/m = ac^{1/n}$ (for discussion see p. 101), and the order of adsorbability is expressed in $a \times 10^4$. The order is the same as in Table VI for ions common to both series but there is no close parallelism between adsorbability and solubility. Formate is adsorbed more strongly than nitrate although the nitrate is much less soluble. Perchlorate likewise is very much out of place, its adsorption being similar to that of chloride and much greater than that of bromide or iodide although its solubility in 50% ethyl alcohol is greater than that of the halides. Karaoglanow [81] found that the contamination by various anions is related to the solubility of the corresponding barium salt and that of cations to the solubility of the corresponding sulfate. He attributes the contamination to secondary chemical precipitation rather than to adsorption.

Although chemically dissimilar ions of the same valence may show a wide variation in the degree of adsorption, thus indicating that adsorbability is a specific property of ions, the similarity in the adsorption of nitrate and nitrite ions, which are more nearly related chemically, suggests that the adsorption of ions by a given disperse phase is determined by two factors: the valence of the ion, and the specific adsorbability of the ion, which is influenced by the solubility of the salt formed with the opposite ion of the crystal lattice, and the radius

[81] Z. physik, Chem., **A178**, 143 (1937).

and deformability of the ion (*cf.* p. 128). By choosing a series of ions of much the same general character, thus minimizing the specific factor, it is possible to emphasize the effect of valence. This is well illustrated by the series of cyanides, the order of adsorption of which is: $Fe(CN)_6^{----} > Fe(CN)_6^{---} > CN > CNS$.

It should be pointed out that data on adsorption of various ions by barium sulfate will be strictly comparable only when the conditions of precipitation, the size of the particles of the adsorbent, the ions in excess, etc., are constant. De Brouckère [82] found, for example, that, under conditions of adsorption entirely different from those described above, the order of adsorption of the halides is: I > Br > Cl. This is the reverse of what would be predicted by Paneth-Fajans' rule but is the order of decreasing size and deformability of the halogen ions.

Referring to Table VI, it will be seen that the adsorption is very much greater when the precipitation is carried out with barium ion in excess than with sulfate ion in excess. This was attributed by Weiser and Sherrick to the well-known difference in the physical character of the particles precipitated under the two sets of conditions; but from observations on adsorption by calcium oxalate Kolthoff and Sandell [83] concluded that, in general, the occlusion of foreign ions by internal adsorption is always greater on precipitation in the presence of an excess of a lattice cation than in the presence of an excess of a lattice anion.

Contamination by Potassium Permanganate and Barium Nitrate. The precipitation of barium sulfate in the presence of potassium permanganate is said by Grimm [84] to give well-defined mixed crystals of a red color which are not decolorized by being warmed with oxalate for two months. Grimm and Wagner [85] obtained precipitates containing as much as 80 mol per cent potassium permanganate and showed the relationship between the permanganate composition of the crystals C_{cr} and the solution from which they separate C_s to be given by the expression $C_{cr} \cong kC_s$. Moreover, Wagner showed that the x-ray diffraction lines of barium sulfate are displaced toward the lines of the isomorphous potassium permanganate, in proportion to the permanganate content of the crystals. The samples were prepared by pre-

[82] J. chim. phys., **27**, 543 (1930).

[83] J. Phys. Chem., **37**, 443, 459 (1933).

[84] Z. Elektrochem., **30**, 467 (1924); Naturwissenschaften, **15**, 561 (1927); *cf.* Hüttig and Menzel: Z. anal. Chem., **68**, 343 (1926).

[85] Z. physik. Chem., **132**, 131 (1928); Wagner: **B2**, 27 (1929).

cipitation at 50° in the presence of potassium permanganate, centrifuging and washing with water, which gave compositions below 8 mol per cent permanganate. Higher concentrations were obtained by washing with acetone only; and the highest concentrations by not washing at all. The samples were dried in vacuum at 110–120° C. Similar observations with a sample of barium sulfate containing 15.7 mol per cent barium nitrate gave no apparent displacement of the barium sulfate diffraction lines.

The above observations would appear to offer conclusive evidence that potassium permanganate forms mixed crystals with barium sulfate.[86] Balarew and coworkers[87] are equally certain that the potassium permanganate is held by adsorption on the inner surface of the barium sulfate crystals. A product colored similarly to that of Grimm is obtained by allowing potassium sulfate in saturated potassium permanganate to diffuse through a porous cup into barium chloride solution saturated with potassium permanganate; but this product is completely decolorized by washing with oxalate and at the same time breaks up into minute prisms. Since mixed crystal formation should not be prevented by a change in the velocity of crystallization, the obvious conclusion is that the red precipitate is not homogeneous but consists of minute prisms of barium sulfate colored by adsorbed permanganate. A freshly precipitated sample of barium sulfate takes up permanganate that is not removed by prolonged contact with solutions of sulfurous acid, oxalic acid, or hydrogen peroxide.[88] The amount of permanganate taken up decreases with the age of the barium sulfate, and a well-aged sample is not colored at all in contact with the permanganate solution. These and other facts support the view that the permanganate is held by adsorption on the inner surfaces of barium sulfate, and not in solid solution. The most convincing argument in support of the solid-solution theory is the apparent displacement of the x-ray diffraction lines observed by Wagner; but Balarew[89] considers this evidence to be misleading. The samples which Wagner examined contained a large amount of potassium perman-

[86] *Cf., also,* Karaoglanow and Sagortschev: Z. anorg. Chem, **221,** 369; **222,** 249 (1935).

[87] Balarew · Z anorg. Chem., **156,** 301 (1926); Balarew and Kaischew: **167,** 237; **168,** 154 (1927); Balarew and Kandilarow: **162,** 344 (1927); Balarew: **169,** 257 (1928); Balarew, Kaischew, and Srebrow **174,** 295 (1928); *cf.* Koluschewa and Sewrugowa: Kolloid-Z., **60,** 141 (1932).

[88] *Cf.* Geilmann: Z. anorg. Chem., **159,** 271 (1926); Kolthoff and Sandell: J Phys. Chem., **37,** 723 (1933).

[89] Balarew and Lukowa: Kolloid-Beihefte, **32,** 304 (1931).

ganate entrained in vacuoles in the precipitate. Balarew thinks that, when the precipitates are dried in vacuum at 120°, the excess permanganate crystallizes on the surface of the barium sulfate crystals, making layers of crystals of two different compounds that will give an x-radiogram slightly different from either. If this be true, then

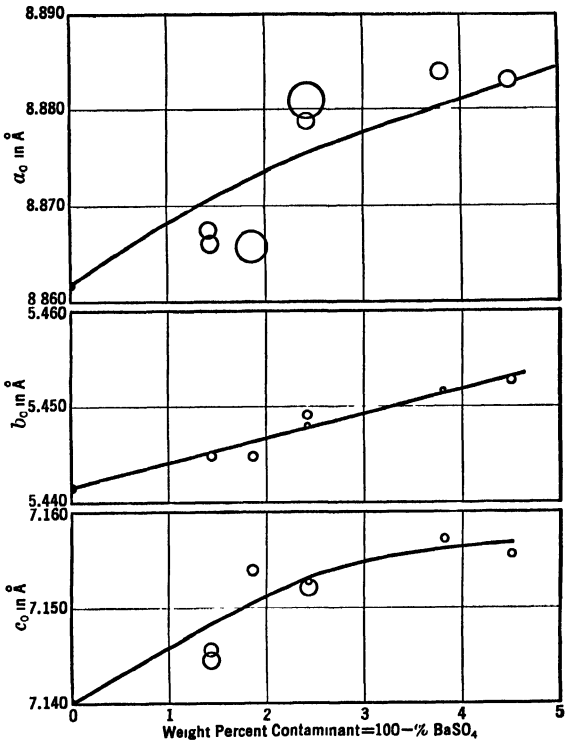


FIG. 4—Effect of permanganate contamination on the lattice parameters of barium sulfate crystals.

the x-radiogram of undried samples of barium sulfate containing permanganate should be identical with that of pure barium sulfate. That they would not be exactly the same is indicated by Averell and Walden's [90] results of an x-ray study of permanganate-contaminated crystals prepared by Grimm and Wagner's procedure, in the absence of all foreign ions except permanganate and hydrogen. In Fig. 4 are

[90] J Am. Chem Soc., **59**, 906 (1937).

plotted the lattice parameters $a_0b_0c_0$ in Ångström units against the weight percentage of total contaminant (water + $HMnO_4$) present in the crystals. The radii of the circles around the experimental points are the probable errors determined by the least squares analysis of the films. The lattice parameters vary more regularly with the percentage of total contaminant than with the percentage of permanganic acid alone, indicating that the expansion of the lattice is caused by the entry of both permanganic acid and water in varying degrees. Since the lattice parameters vary with increasing percentage of contaminant, the solid-solution character of the precipitates is indicated. This does not mean that all or even the largest percentage of contaminant is held in solid solution. Since the increase in the lattice parameters is small, it may be that most of the foreign material is held by adsorption.

From a phase-rule study of the system $BaSO_4$-$KMnO_4$, Benrath and Schackmann [91] found that no solid solution of the two constituents exists in equilibrium with the mother liquor. There is, however, no reason to believe that the precipitates prepared by Grimm and Wagner are the result of heterogeneous equilibria but rather of kinetic processes localized at the surface of the growing crystal.

In this connection Walden and Cohen [92] made a precise x-ray study of barium sulfate contaminated with barium nitrate and came to the conclusion that a part at least of the nitrate was held in solid solution. The data using calcium radiation are summarized in Fig. 5, which shows the relation between the lattice parameters (accurate to less than 0.01%) and the nitrate content of the crystals. This orderly variation of the lattice spacing with the nitrate content, as well as an observed increase in volume of the unit cell of the contaminated barium sulfate, indicates that the foreign ions have actually entered the lattice giving a solid solution. But, as already pointed out, the formation of a solid solution does not exclude surface adsorption as a contributing factor in the contamination. Indeed, Schneider and Rieman, III,[93] attribute the contamination by nitrate chiefly to adsorption and the contamination by nitrite chiefly to solid-solution formation. In support of this they showed that: (1) the excess of lattice ion influences the coprecipitation of nitrite ion much less than it does that of iodide, bromide, chloride, nitrate, and chlorate; (2) confirming the observations of Weiser and Sherrick, all the above ions except

[91] Z. anorg. Chem., **218**, 139 (1934)
[92] J. Am. Chem. Soc., **57**, 2591 (1935).
[93] J. Am. Chem. Soc., **59**, 354 (1937).

nitrite follow Paneth-Fajans' rule; (3) the crystal size is decreased much less by the carrying down of nitrite than of the other ions; (4) the nitrite ion is removed by digestion more slowly than the other ions. In the light of these observations it is still an open question to

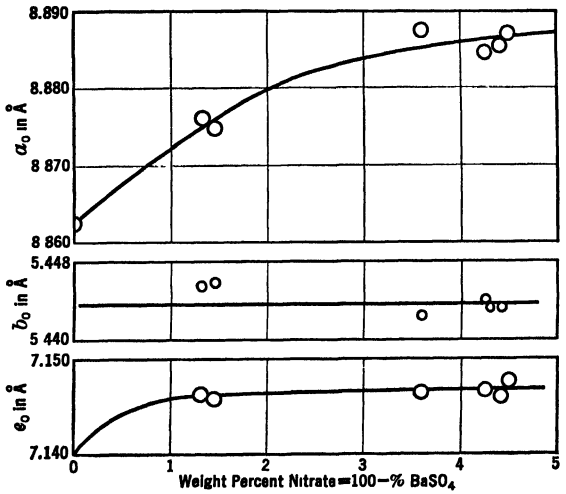


FIG. 5.—Effect of nitrate contamination on the lattice parameters of barium sulfate crystals.

what extent the contamination by nitrate as well as by permanganate is due to adsorption and to what extent to solid solution.

Adsorption of Organic Ions

Studies on the adsorption of organic substances by barium sulfate contribute nothing especially new. Thus Rossi and Scandellari [94] showed that the adsorption of a colloidally dispersed dye like night blue increased with increasing degree of dispersion of the adsorbent and the adsorbed substance. Hel'd [95] showed that electrolytes influence the adsorption of nonylic acid according to well-established rules. For example, a strongly adsorbed cation like barium increases the adsorption of the nonylate anion, and a strongly adsorbed anion like

[94] Gazz chim. ital., **63**, 261 (1933).

[95] Hel'd and Dyachkov: Compt. rend. acad. sci. U.S.S.R., **1**, 193; Hel'd and Samokhvalov: 263 (1934); J. Phys. Chem. (U.S.S.R.), **6**, 1210 (1935); Kolloid-Z., **72**, 13 (1935).

sulfate cuts down the adsorption of the nonylate ion. The adsorption of sodium laurate apparently gives a film two molecules thick on barium sulfate. It is claimed that the first layer is held by chemical attraction and the second by van der Waals' forces. Flotation of barium sulfate by sodium laurate was found to be at a maximum when the first layer was saturated. The heat of adsorption of sodium oleate was estimated as +0.067 cal./g $BaSO_4$.[96] Bartell and Hershberger[97] showed that barium sulfate is more highly wetted by organic liquid than the sulfide pigments (p. 280).

Electrical Properties of Precipitated Barium Sulfate

Gyemant[98] studied the effect of barium ion on the electrokinetic potential, ζ, at the interface of finely ground heavy spar and water. The ζ-potential was determined from electroendosmotic data by substituting in the formula:[99]

$$\zeta = \frac{4\pi\eta M}{DI\sigma}$$

where η is the viscosity at room temperature, M the volume of liquid transferred through the diaphragm in unit time, D the dielectric constant, I the current strength, and σ the specific resistance of liquid. Since the solubility product of barium sulfate is 10^{-10}, it follows that $p\text{Ba} + p\text{SO}_4 = 10$, where $p\text{Ba}$ is the negative logarithm of the barium ion concentration. The sample of barium sulfate was negative in pure water; at $p\text{Ba} = 7$, *i.e.*, 0.001 N Na_2SO_4, the cataphoretic velocity and hence the ζ-potential was zero This, therefore, represents the point of change of sign of the potential. The small positive potential remains almost constant to $p\text{Ba} = 4$ then falls rapidly to a minimum at $p\text{Ba} = 2$. Kruyt and Ruyssen[100] likewise showed that natural barite possesses an appreciable negative charge in pure water. The sign of the potential depends, however, on the extent of surface: natural barite of particle size 150μ in diameter has a larger negative potential than precipitated particles 20–40μ in diameter; and particles around 10μ have only a very slight negative potential which is changed

[96] Hel'd and Khainskii: Kolloid-Z, **75**, 287 (1936).
[97] Ind. Eng. Chem, **22**, 1304 (1930)
[98] Z physik Chem, **103**, 260 (1922)
[99] *Cf.* Freundlich: "Kapillarchemie," 2nd ed., 331 (1922).
[100] Proc. Acad. Sci. Amsterdam, **37**, 624 (1934); Oyama: J. Chem Soc. Japan, **54**, 582 (1933).

to positive with a trace of barium chloride, because of the strong adsorption of barium ion. The potential is always negative in sulfate solution on account of the strong adsorption of sulfate ion [101] Some data showing the relative effect of barium chloride and sodium sulfate on the ζ-potential are given graphically in Fig. 6. Chlorides of the bivalent metals and aluminum give a positive ζ-potential to the particles because of stronger adsorption of cations than of the anion. If the ζ-potential is a measure of the adsorption of the cations, the metals arrange themselves in the order: Al > Sr > Ca > Zn >

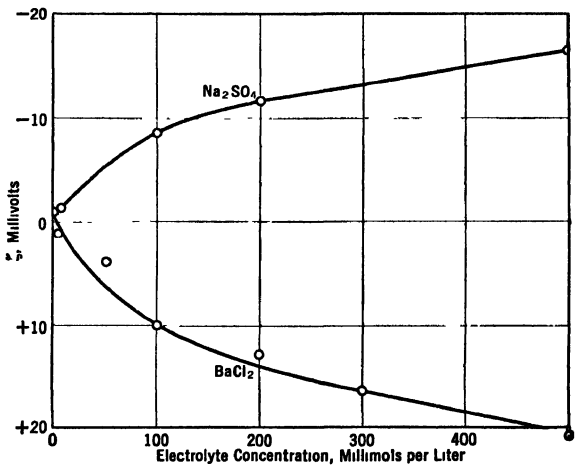


FIG 6.—Effect of barium chloride and sodium sulfate on the ζ-potential of barium sulfate

Mg > Cd. This is not the same as the order of adsorption given above (p. 29).

It is a simple matter, by means of Congo red, to differentiate between colloidal particles or crystals that are positively charged owing to preferential adsorption of barium ion and those that are negatively charged owing to preferential adsorption of sulfate ion.[102] The positively charged particles adsorb the Congo red anion giving a red to deep violet-red precipitate; the negatively charged particles are not colored at all. At a *p*H of 3.3–3.5, a blue precipitate is obtained

[101] *Cf*, *also*, Mattson· J Phys. Chem, **32**, 1532 (1928).
[102] Riegel and Riddson· Kolloid-Z, **64**, 304 (1933).

which consists of a mixture of the blue Congo acid and colorless crystals of barium sulfate.

Barium Sulfate Sols

Preparation

Von Weimarn obtained momentary sols of barium sulfate by mixing solutions of barium thiocyanate and manganese sulfate of approximately 0.0008 normality. In spite of the dilution, the particles agglomerate and settle out in a short time. Kato [103] diluted a *M* H_2SO_4 solution with twice its volume of alcohol and added it to an equivalent amount of *M* $Ba(C_2H_3O_2)_2$ diluted with 5 times its volume of alcohol. On evaporating the resulting gelatinous precipitate and milky sol to dryness under reduced pressure below 40°, a translucent casein-like residue was obtained which was readily and completely dispersed in water to a stable fluorescent sol. The sol was positively charged and showed the usual precipitation reaction towards anions. Cations of high valency stabilized the sol, barium chloride and nitrate precipitating it only at high concentrations. Thorne and Smith [104] prepared a similar sol using methyl instead of ethyl alcohol, and Recoura [105] mixed equivalent solutions of barium ethylate and sulfuric acid in pure glycerol followed by dilution with water.

Since the charge on the barium sulfate particles becomes negative when the sulfate ion concentration of the surrounding liquid is above 0.001 *M*, it should be possible to prepare a stable negative sol in the presence of sulfate or other readily adsorbed anion. Such a sol is obtained by adding a slight excess of 0.1 *N* K_2SO_4 to 0.1 *N* $BaCl_2$ using as solvent 1 part of water to 5 parts of glycerol.[106] A negative hydrosol is also obtained by double decomposition of barium salts and sulfates in the presence of sodium citrate. Such sols are almost clear, and Spiller [107] believed them to be true solutions of a double salt of barium sulfate and citrate. Nichols and Thies [108] showed, however, that the apparent solutions are merely negatively charged dispersions of barium sulfate in which the particles are in an

[103] Mem. Coll. Sci., Kyoto Imp. Univ., **2**, 187 (1909-10); Lott: J. Am. Pharm Assoc., **17**, 454 (1928).

[104] Kolloid-Z, **42**, 328 (1927).

[105] Compt. rend., **146**, 1274 (1908).

[106] Weiser: J Phys. Chem., **21**, 318 (1917).

[107] J. Chem. Soc, **10**, 110 (1858).

[108] J. Am. Chem. Soc., **48**, 303 (1926).

extremely fine state of subdivision. Quantitative estimations involving the precipitation of barium sulfate can be made in the presence of citrates, provided slightly more than enough acid is added to convert the citrates into citric acid, thereby cutting down the concentration of citrate ion below the point necessary for peptization of barium sulfate.

Feilmann [109] prepared a sol of barium sulfate by precipitation in a slightly alkaline solution of commercial casein. Since the reaction of the sol towards acid and alkalis is that of casein, it is obvious that the colloidal barium sulfate is surrounded by a protecting film of proteid. The hydrous oxides of iron, aluminum, chromium, and thorium are adsorbed by colloidally dispersed barium sulfate particles giving stable sols.

Properties

The sols of barium sulfate are faintly opalescent to distinctly milky in appearance, depending on the concentration and the size of particles. Bechhold and Hebler [110] investigated nephelometrically the connection between turbidity and the size of suspended particles of barium sulfate in various mixtures of ethyl alcohol and glycerol. For suspensions containing the same amount of barium sulfate, but of varying degrees of dispersion, the turbidity increases from 2.5 μ downwards. The maximum turbidity is reached with particles of about 800 mμ for white light, that is, the region of the extreme red. Further reduction of particle size causes a marked decrease in turbidity. Rayleigh's law, $I = K(nv^2/\lambda^4)$, in which I is the intensity of the scattered light, n the number of particles per unit volume, v the volume of the particles, λ the wave length of the light, and K a constant, holds only for the region of size below 800 mμ. If a standard sol of known turbidity is available, it is possible to estimate the size of amicrons and submicrons from the relation between turbidity and particle size.

Owe [111] showed that the turbidity of barium sulfate sols, as measured by the nephelometer, is different for particles of the same size formed in glycerol-water and glycerol-alcohol mixtures. The difference is probably due to variations in crystalline form and in the refractive indices of the salt thrown down in the different media. The

[109] Chem. News, **98**, 310 (1908).
[110] Kolloid-Z., **31**, 70 (1922).
[111] Kolloid-Z., **32**, 73 (1923).

turbidity in such mixtures is a maximum with particles around 200 mμ in reflected light, and around 1000 mμ in transmitted light.

Svedberg and Nichols [112] investigated the size and distribution of size of particles by a centrifugal method for barium sulfate sol prepared by the interaction of 0.1 *N* $Ba(SCN)_2$ and 0.1 *N* $(NH_4)_2SO_4$ in the presence of potassium citrate.

[112] J. Am. Chem. Soc., **45**, 2910 (1923); *cf.* Nichols and Liebe: Colloid Symposium Monograph, **3**, 268 (1925).

CHAPTER III

COLLOIDAL SULFATES OF LEAD AND STRONTIUM

COLLOIDAL LEAD SULFATE

Lead sulfate cannot be thrown down as a transparent jelly from aqueous solution like barium sulfate, which is only one-fifteenth as soluble It can be obtained in the sol state by mixing solutions of lead nitrate and sulfuric acid as dilute as 0 005 *N*. With a small excess of lead nitrate, the particles are positively charged by selective adsorption of lead ions; and, with a small excess of sulfuric acid, the particles are negatively charged by selective adsorption of sulfate ions.[1] In the absence of protecting colloids, the sol coagulates in a short time; but Leuze [2] prepared a stable sol by treating a mixed solution of lead acetate, sodium hydroxide, and sodium "protalbinate" with a solution of sodium sulfate. On dialysis, the protected brown sol which first formed became gradually opalescent and milky.

Colloidal Behavior of Lead Sulfate in the Storage Battery. In the lead storage battery, both the spongy lead and lead peroxide plates are formed in sulfuric acid solution. The first step in forming the lead peroxide plate consists in the precipitation of colloidal lead sulfate which is negatively charged and so is carried to the lead anode. The sulfate is held on the anode by the cataphoresis effect and to a certain extent by adsorption, in a condition for the second step, the oxidation to peroxide. If an alternating current is passed between lead electrodes, lead sulfate formed at one moment is carried away by cataphoresis on the reversal and at both electrodes, resulting in a precipitate of lead sulfate at the bottom of the container. No appreciable amount of lead peroxide is formed using a fairly rapid alternating current, indicating that adsorption of lead sulfate by the lead grid is of minor importance in comparison with the cataphoresis effect. As is well known, this is not true in the slow reversals of

[1] Jewett: J. Phys Chem, **33**, 1024 (1929).

[2] "Zur Kenntnis Kolloidaler Metalle und ihrer Verbindungen," Erlangen, 21 (1904).

actual practice: when the spongy lead plate of the battery is converted in part into lead sulfate on discharge, the sulfate is not carried away by cataphoresis when the discharged plate is made cathode, but is reduced back to spongy lead. Similarly, when a spongy lead plate is formed by alternate oxidation and reduction, the sulfate formed on the oxidation is reduced to lead when the current is reversed and is not carried away by cataphoresis. The differences in behavior on rapid reversals and slow reversals of the current indicate that lead sulfate on the surface of lead changes with time so that the tendency of the particles to move to the anode in sulfuric acid solution is negligible compared to other factors. Since suspended lead sulfate formed in sulfuric acid moves to the anode hours after its preparation, Jewett [1] believes the important factor to be an increased adherence to the lead. It is probable that with time an oriented adsorption of lead sulfate on lead takes place with the result that the sulfate is held more firmly to the lead. The relatively large crystals of aged lead sulfate in the plates of a "sulfated" battery are very difficult to oxidize and reduce at the respective electrodes.

Adsorption on the Lead Sulfate Lattice

Extent of Surface from Adsorption Measurements

An ionic precipitate such as lead sulfate is in kinetic equilibrium with the surrounding solution, the speed with which the ions leave the surface being equal to the speed with which the ions from the solution deposit on the surface. Paneth [3] used this principle in determining the specific surface of lead sulfate from measurements of the adsorption of thorium B, an isotope of lead. Paneth's fundamental equation representing the distribution when kinetic exchange equilibrium is established is:

$$\frac{\text{Isotope (surface)}}{\text{Isotope (solution)}} = \frac{\text{Element (surface)}}{\text{Element (solution)}} \qquad (1)$$

from which he derived the following expression for calculating the specific surface in terms of grams of lead on the surface of 1 g of $PbSO_4$, from data on the adsorption of thorium B:

$$\text{Specific surface} = \frac{\text{ThB adsorbed in \%}}{100 - \text{ThB adsorbed in \%}} \cdot \frac{\text{g Pb in solution}}{\text{g } PbSO_4} \qquad (2)$$

[3] Physik. Z., **15**, 924 (1914); Paneth and Vorwerk: Z. physik. Chem., **101**, 445 (1922).

In a given aged sample of $PbSO_4$, Paneth and Vorwerk obtained the value 6.4×10^{-4} g Pb for the specific surface, allowing 3 minutes' shaking time for equilibrium to be set up. Equilibrium is not reached entirely even after 30 minutes' shaking, probably because of the slowness with which agglomerates are broken up by shaking. Kolthoff and Rosenblum [4] found that an hour was required to set up kinetic exchange equilibrium in aged samples and obtained a value for the specific surface of 8.4×10^{-4} g Pb for a sample having the same average size of crystals as Paneth and Vorwerk's sample. This means that there are $(8.37 \times 10^{-4})/207 \times 6.06 \times 10^{23} = 24.5 \times 10^{17}$ lead ions in the surface of 1 g of $PbSO_4$. Assuming that the crystals are cubic and have a density of 6.23, there are 2.32×10^{7} molecules of $PbSO_4$ per cm, and the size of 1 molecule $= 4.32 \times 10^{-8}$ cm; hence the surface per molecule is $(4.32 \times 10^{-8})^2 = 18.6 \times 10^{-16}$. The specific surface is therefore $18.6 \times 10^{-16} \times 24.5 \times 10^{17}$ cm^2 = 45.5 dm^2. The area measured microscopically was found to be 33.4 dm^2, confirming Paneth's observations that the two methods show good agreement, considering the errors in the microscopic measurements.

The adsorption of dyes such as Ponceau 2R,[5] methylene blue, Ponceau 4R,[6] and wool violet 4BN[7] has been used as a measure of the specific surface of lead sulfate. Of these, wool violet appears to be especially suitable since the surface of lead sulfate is saturated at relatively small concentrations of the dye in the supernatant liquid and the lead salt of the dye is sufficiently soluble to permit a study of the dye adsorption in the presence of a slight excess of lead ions in solution.

The change in the specific surface with time can be followed by means of adsorption measurements. Fresh precipitates of compounds like lead sulfate consist of very imperfect crystals and possess an internal surface of fine capillaries and canals which is much greater than the external surface. On aging, the crystals rapidly become more perfect which results in a rapid decrease in the internal surface, whereas the external surface decreases but very slowly. Kolthoff and Rosenblum [8] showed that the external surface may be estimated by

[4] J. Am. Chem. Soc., **55**, 2656 (1933)

[5] Paneth and Vorwerk: Z. physik. Chem., **101**, 480 (1922); Paneth and Thimann: Ber., **57B**, 1215 (1924).

[6] Kolthoff and Rosenblum: J Am. Chem. Soc, **55**, 2664 (1933).

[7] Kolthoff, von Fischer, and Rosenblum: J. Am Chem. Soc., **56**, 832 (1934).

[8] J. Am. Chem. Soc., **56**, 1264, 1658 (1934); Phys. Rev., **45**, 341 (1934).

determining the adsorption of wool violet after short intervals of shaking with the dye since the large size of the dye molecules does not allow penetration into the fine capillaries of the internal surface. The sum of the external and internal surfaces may be obtained by measurements of the adsorption of thorium B from a radioactive lead nitrate solution. The speed of distribution of the thorium B from such a solution was found to be independent of the rate of shaking as long as the precipitate was not allowed to settle.[9]

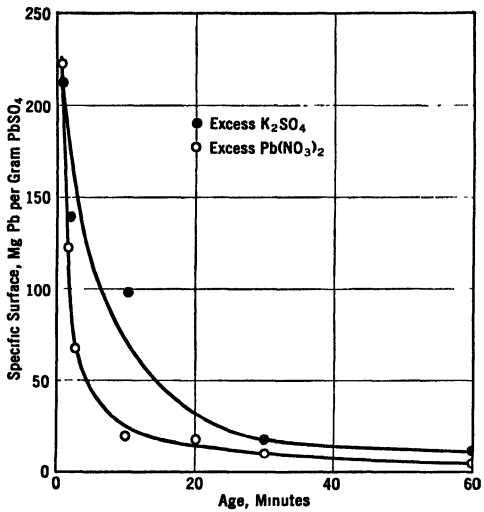


FIG 7.—Rate of decrease of specific surface of lead sulfate in the presence of a slight excess of potassium sulfate and lead nitrate, respectively.

The specific surface of a precipitate freshly formed at room temperature is very large, amounting to approximately 700 mg Pb per g $PbSO_4$. Since 1 g of $PbSO_4$ can contain, at most, 683 mg of lead ions, it is obvious that the thorium B distributes itself uniformly throughout the fresh precipitate in spite of the fact that the crystals appear compact on microscopic observations.

The porous mass ages rapidly, the specific surface decreasing 20 to 40 times after one hour. Some observations on the rate of decrease of specific surface are shown graphically in Fig. 7 for a sample precipitated with a slight excess of lead nitrate and one precipitated with a slight excess of potassium sulfate. The final state of the aging

[9] Kolthoff and Rosenblum: J. Am. Chem. Soc., **58**, 121 (1936).

process is reached very slowly, requiring several days as evidenced by microscopic observations of increasing particle size and by the decreasing adsorption of wool violet. The very rapid aging immediately following the precipitation results in a perfection of the primary crystals; on longer standing, a slow crystal growth occurs as a secondary process. The speed of aging is independent of the amount of precipitate, the amount of lead in solution (the lead concentration being constant), and of stirring. The rapid aging is not due to an Ostwald ripening process in which larger particles grow at the expense of smaller ones since speed of agitation would influence such a process. The recrystallization responsible for the aging and perfection of the crystals apparently takes place at great speed in a liquid layer around the particles. The fresh precipitate does not age in alcohol, in which it is insoluble, and external crystallization does not take place if the fresh precipitate is coated with an adsorbed film of wool violet.[10] Moreover, the adsorption of dyes such as Ponceau 4R and wool violet inhibits greatly the speed of the kinetic interchange at the interface lead sulfate-solution. As would be expected, the degree of perfection of crystals and the rate of aging are influenced by the concentration of the interacting solutions and by the temperature during precipitation. In accord with the usual rule, a precipitate obtained from 0.025 *M* solutions is much more perfect and coarser than one obtained from 0.1 *M* solutions.[11]

Bancroft and Barnett[12] questioned Paneth's method of determining the specific surface from measurements of the adsorption of dyes, since this adsorption is a function of the apparent *p*H of the solution. They showed, for example, that the adsorption of the basic dye methylene blue by lead sulfate was greater the higher the *p*H value. Similarly Kolthoff, von Fischer, and Rosenblum found the adsorption of the acid dye wool violet to be much greater from an acid medium than from a neutral medium, and to increase with the acidity. These examples are in accord with the rules proposed by Bancroft[13] and demonstrated with several dyes by Briggs and Bull.[14] The variation in the amount of dye taken up at varying *p*H may result in part from the influence of the added acid or base on the dye itself, changing the

[10] Kolthoff and Rosenblum: J Am Chem. Soc, **57**, 597, 607 (1935); **58**, 116, 121 (1936); Phys Rev, **47**, 631 (1935).

[11] Kolthoff and Rosenblum· J. Am. Chem. Soc., **57**, 2577 (1935).

[12] Colloid Symposium Monograph, **6**, 73 (1928).

[13] J Phys Chem., **18**, 1, 118, 385 (1914); **19**, 50, 145 (1915).

[14] J. Phys. Chem., **26**, 845 (1922).

soluble dye salt to insoluble dye acid as upon the addition of acid to Congo red, or from the conversion of soluble salt to insoluble dye base such as takes place on adding sodium hydroxide to methylene blue. These complications merely emphasize the importance of taking the *p*H value into account in adsorption studies with dyes.

In this connection, Kolthoff and Rosenblum [6] showed that, in accord with the usual behavior (p. 106), the adsorption of the acid dye Ponceau 4R by lead sulfate is increased by the addition of the strongly adsorbed lead cations and is decreased in the presence of the strongly adsorbed sulfate anions.

Mechanism of the Adsorption

Exchange Adsorption. As already pointed out, when an ionic precipitate such as lead sulfate is brought in contact with a solution, a kinetic equilibrium is set up between lattice ions in the surface and foreign ions in the solution. For the adsorption of ThB on lead sulfate the distribution is given by Paneth's equation:

$$\frac{\text{ThB (adsorbed)}}{\text{ThB (solution)}} = \frac{\text{Pb (surface)}}{\text{Pb (solution)}} \tag{3}$$

Let x = the amount of the element to be adsorbed, originally present in the solution; y = the amount adsorbed; z = the amount remaining in solution, then $x = y + z$; and O = the amount of the element on the surface of the powder. Substituting in the Paneth equation:

$$\frac{y}{x - y} = \frac{O}{x} \tag{4}$$

from which

$$y = \frac{O \cdot x}{O + x} \tag{5}$$

By means of this equation, Paneth and Vorwerk attempted to calculate the amount of lead ions adsorbed on the surface of an aged lead sulfate. For example, a preparation having a specific surface of 1.29 mg Pb per g $PbSO_4$, adsorbed 0.5 mg Pb^{++} ions when suspended in water (saturated $PbSO_4$ solution) and 1.2 mg Pb^{++} ions when suspended in a solution of $Pb(NO_3)_2$ 0.005 N and above. These figures would indicate that, in the suspension in water, about 40% of the surface is covered by adsorbed lead ions, and that in 0.005 N $Pb(NO_3)_2$ the surface is approximately covered with a monomolecular layer of lead ions.

Kolthoff and Rosenblum[4] confirmed Paneth and Vorwerk's observations that the specific surface was the same in lead nitrate solutions as in water and showed further that it was the same in potassium sulfate solutions as in water. This could not be true if there were any appreciable adsorption of lead and sulfate ions by the aged lead sulfate. It must therefore be concluded that the equation used by Paneth and Vorwerk to calculate the adsorption of lead ions is not correct. Kolthoff and Rosenblum point out that the distribution equation is:

$$\frac{\text{ThB (surface)}}{\text{ThB (solution)}} = \frac{\text{Total Pb (surface)}}{\text{Total Pb (solution)}}, \qquad (3a)$$

where Total Pb (solution) represents the concentration of the lead analytically determined and Total Pb (surface) is the specific surface determined as described above. An adsorption of lead ions from lead nitrate solution would result in an increase in the concentration of lead at the surface and hence an increase in the specific surface. Since the specific surface undergoes little or no change in lead nitrate solutions, it must follow that no measurable adsorption of lead from lead nitrate takes place on the aged precipitate. The same applies to the adsorption of sulfate from sodium sulfate solutions. There must be some adsorption, although it is not measurable, since even aged lead sulfate has a positive charge in lead nitrate solution and a negative charge in sodium sulfate solution. This adsorption appears to be limited to the edges and corners of the crystals and is therefore quite small in aged precipitates. The adsorption would be expected to be much larger in freshly formed precipitates with an irregular and higher specific surface.

When an ionic precipitate is brought in contact with any solution containing a strongly adsorbed ion, an exchange adsorption between the lattice ion and the foreign ion takes place similar to that between lead and ThB considered above. An exchange of this nature is not limited by the similarity in size of the exchanging ion and the exchanged lattice ion. Kolthoff and Rosenblum[15] showed that, in the adsorption of the sodium salts of Ponceau 4R and wool violet, only the dye anions are adsorbed, no sodium ions being removed from solution; and for each adsorbed dye anion an equivalent amount of sulfate is sent into solution. This recalls the adsorption of acid dyes by hydrous oxide mordants where the adsorbed dye anion displaces an

[15] J. Am. Chem. Soc., **55**, 851, 2664 (1933); **56**, 834 (1934).

equivalent amount of adsorbed chloride from the surface of the hydrous oxide and no sodium ion is adsorbed.[16]

Other Mechanisms. Although the adsorption of acid dyes by lead sulfate is probably best interpreted as an exchange adsorption, other mechanisms are possible.[17] For example, it may be argued that wool violet is adsorbed as lead salt on the surface of lead sulfate, the lead ions being furnished by the saturated solution of lead sulfate. The solution is no longer saturated, and accordingly more lead sulfate will go into solution until equilibrium is restored. The final result is that equivalent amounts of lead and wool violet ions are removed from the solution, leaving it with sulfate ions in excess. Another mechanism which involves neither exchange nor adsorption of the lead salt of wool violet assumes that a triple layer is formed, the dye ions being truly adsorbed on the surface.[18] Since the thermodynamic potential of the precipitate is scarcely changed by the adsorption, some lead ions are adsorbed on the surface but most will be present as counter ions.

In this connection, Kolthoff points out that, if an ion foreign to the lattice ion gives a marked exchange with the lattice ion of the same electrical sign in the surface, it cannot be concluded from the experimental data that an equivalent adsorption of lattice ion and foreign ion has taken place although equivalent amounts of lattice ion and foreign ion are removed from solution. The foreign ion may disappear by exchange and the lattice ion by precipitation in the form of the adsorbent itself. For example, in the adsorption of the lead salt of wool violet, the primary reaction is: $PbSO_4$ + wool violet$--$ → Pb-wood violet + SO_4--. The exchanged sulfate ions are precipitated as lead sulfate by the excess lead ions in solution. Taking the analytical results, one might conclude that the lead salt of wool violet is adsorbed when as a matter of fact the wool violet ions are removed by exchange and the lead ions by precipitation. A similar behavior is probably encountered in the adsorption of calcium iodate by calcium oxalate.[19]

COLLOIDAL STRONTIUM SULFATE

The solubility of strontium sulfate in water (0.00062 mol/l) is more than twice as great as that of lead sulfate; hence it is obtained

[16] Weiser and Porter: J. Phys. Chem., **31**, 1824 (1927).
[17] Kolthoff: J. Phys. Chem., **40**, 1027 (1936).
[18] Verwey: Kolloid-Z., **72**, 187 (1935).
[19] Kolthoff and Sandell: J. Am. Chem. Soc., **55**, 2170 (1933).

in the colloidal state only by precipitation in alcohol-water solution.[20] Sols in 75% or more of alcohol, and containing 0.6 g $SrSO_4$/l, possess but a slight opalescence when first formed and are stable for months. By working with concentrated solutions, gelatinous precipitates or jellies are obtained consisting of interlocking bundles of needle-shaped crystals.

Mechanism of the Precipitation Process

Odén[21] studied the mechanism of the precipitation of strontium sulfate by measuring the conductivity of solutions which result from mixing measured amounts of strontium hydroxide and sulfuric acid. It was found that the first stage in the process, the formation of nuclei, can be represented by the equation

$$n = \text{const. } C_1 \cdot C_2 t^{\alpha},$$

in which n is the number of nuclei, C_1 and C_2 are the concentrations of the reacting ions, t is the time, and α is a number greater than 3 and dependent on the number of ions in the unit cell. This confirms von Weimarn's view concerning the relationship between particle size and the concentration of reagents. In further accord with von Weimarn's theory, the second stage in the process consists in the growth of nuclei which is followed by an aggregation of the primary particles into secondary aggregates analogous to the coagulation of sols, and finally by the growth of larger crystals at the expense of smaller ones. The conductivity of the solution supersaturated with respect to the precipitate was found to be constant at first for a considerable period of time, the length of which is determined by the concentration of the base and acid. After this interval, the conductivity decreases gradually during the process of actual precipitation until it reaches a minimum value corresponding to complete precipitation. This process requires several hours in concentrations of 0.02 to 0.06 N but only a few minutes in more concentrated solutions. The rate of growth of single crystals (primary particles) in a supersaturated solution and in a non-aggregated state (*cf.* p. 12) may be expressed by the equation $V_k = K \cdot O_t \cdot (C_t - C_m)$, where V_k is the velocity of crystallization;

[20] Von Weimarn: Repts. Imp. Research Inst., Osaka, Japan, **9**, 13 (1928); **12**, 117 (1931); *cf., also,* "Die Allgemeinheit des Kolloidzustandes," Dresden (1925).

[21] Arkiv Kemi, Mineral. Geol., **9**, No. 23 (1925); Odén and Werner: **9**, No. 32 (1926).

O_t, the total surface of the crystals at time t; C_t and C_m, the concentration of the solution at time t and at saturation, respectively; and K, a constant.

The observations and conclusions of von Weimarn and of Odén concerning the mechanism of the precipitation process were confirmed and extended by Lambert and Hume-Rothery,[22] who worked with solutions varying in concentration between 0.01 and 3.47 *N*. Under certain conditions, especially high concentrations and low temperatures, the initial precipitate consists of needle-shaped crystals believed to be a hydrate of strontium sulfate. On standing in the molten liquor the needle crystals go over spontaneously into stable rhombic crystals of anhydrous strontium sulfate which are also formed directly from dilute solutions at low temperatures and from solutions not too concentrated at higher temperatures. The conclusion that the needles are a hydrate and the rhombic crystals are the anhydrous salt is questionable. This could be decided definitely by x-ray examination of the two types of crystals.

Observations of the time which elapsed before a precipitate appears in the presence of different salts led to the conclusion that a positively charged sol is formed as an intermediate stage in the precipitation and that the sol precipitates more or less rapidly depending on the precipitating or stabilizing effect of the other ions. For example, other conditions being the same, a definitely increasing time is required for the appearance of the precipitate, in the presence of cations in the order: $Na < Mg < Al < H$, which is the order of increasing protecting power of cations for positive sols. Similarly, the order of increasing velocity of precipitation of strontium sulfate in the presence of anions is: $CH_3COO > Cl > NO_3$, which is the order of the coagulating power of these anions for positive sols. This point of view accounts for the relative velocities of precipitation of the more concentrated solutions; but, in dilute solutions, other factors such as viscosity play an important part in determining the relative times for the appearance of a precipitate. The size of the particles was found to depend on two main factors: (1) the velocity of precipitation, increase of which leads to smaller primary particles in accord with von Weimarn's theory; and (2) the facility for rapid diffusion which favors larger particles. Similar observations and conclusions were made from a study of calcium sulfate.[23]

[22] J. Chem. Soc., 2637 (1926); *cf.* von Weimarn: 929 (1927).
[23] Lambert and Schaffer: J. Chem. Soc., 2648 (1926).

Campbell and Cook[24] observed the fall in conductivity of supersaturated solutions of strontium sulfate formed by mixing potassium sulfate and strontium chloride solutions. Solutions down to and including 50% supersaturation crystallize spontaneously, but the conductivity never falls to normal. Prior to the formation of microscopic particles, von Weimarn's colloidal zone was observed, but not all the colloidal particles appear to function as nuclei. Apparently a nucleus once formed grows rapidly to considerable magnitude. The interesting observation was made that after the degree of supersaturation has fallen to 40–50%, further precipitation appears to stop or to become very slow.[25] A solution appears to remain permanently supersaturated at 30–40% supersaturation despite the presence of large particles. No experiments were carried out with interacting solutions of sufficiently high concentrations to give the needle-shaped crystals observed by von Weimarn and by Lambert and Hume-Rothery.

Adsorption on the Strontium Sulfate Lattice

Since radioactive isotopes of strontium, calcium, and barium are not known, Paneth's equation in its original form is inapplicable for the estimation of the extent of surface of the alkaline-earth sulfates. In respect to isomorphous substances such as lead sulfate and strontium sulfate, it is assumed that the lead ions in a solution in which strontium sulfate is suspended will enter into kinetic exchange with the outer layer of strontium sulfate. At equilibrium the distribution will be represented by the expression:

$$\frac{\text{Pb (surface)}}{\text{Pb (solution)}} = K \frac{\text{Sr (surface)}}{\text{Sr (solution)}} \qquad (6)$$

in which K represents the distribution coefficient of lead between the solution and the surface of strontium sulfate. As already pointed out, Kolthoff showed the applicability of an equation of this type to the distribution of lead or chromate ions between the surface of barium sulfate and solution (p. 32), and to the distribution of bromide ions between silver chloride and solution. In such cases the foreign ion fits the lattice of the adsorbent and its size is similar to that of the ion replaced. An exchange of this nature is not limited to isomorphous ions or to ions of similar size as evidenced by the results on the distribution of the dye ions between lead sulfate and solution

[24] J. Am. Chem. Soc., **57**, 387 (1935).
[25] *Cf.* Dundon: J. Am. Chem. Soc., **45**, 2658 (1923).

(p. 55). An equation similar to (6) represents the distribution of sulfate or barium ions between calcium oxalate and solution [19] and of eosin [26] and wool violet [17] anions between silver chloride and solution.

For determining the extent of surface of strontium sulfate or barium sulfate which are isomorphous with lead sulfate, the equation of Paneth [27] takes the form:

$$k\frac{\text{ThB (surface)}}{\text{ThB (solution)}} = \frac{\text{Sr (surface)}}{\text{Sr (solution)}} \tag{7}$$

where k is the ratio of solubilities of the sulfates of thorium B and strontium in salt solutions. The value of k was found to be 1/15 when the surface of strontium sulfate is determined from adsorption of thorium B; and 14 when the surface of barium sulfate is estimated by the same method. The applicability of the procedure is evidenced by the similarity between the values estimated microscopically and by the radioactive method. The latter method is not applicable for the determination of the extent of the surface of calcium sulfate since the calcium salt is not isomorphous with the sulfates of thorium B, lead, strontium, and barium.

Kolthoff and MacNevin [28] found that the simplest method of determining the specific surface of barium sulfate is based on the determination of the amount of wool violet adsorbed on the saturated surface of the precipitates; a method based on the exchange between chromate and sulfate [29] ions likewise gives good results; the thorium B method is unsatisfactory except with well-aged precipitates.

[26] Kolthoff: Kolloid-Z., **68**, 190 (1934).
[27] "Radio Elements as Indicators," McGraw-Hill Book Co, 65 (1928).
[28] J. Am. Chem Soc., **58**, 725 (1936).
[29] Kolthoff and Noponen: J. Am. Chem. Soc., **59**, 1237 (1937).

CHAPTER IV

COLLOIDAL CALCIUM SULFATE; PLASTER OF PARIS

The relatively high solubility of calcium sulfate in water precludes the possibility of forming a stable hydrosol; but a dilute fairly stable sol may be prepared in an 86% ethyl alcohol-water mixture.[1] The gelatinous form of calcium sulfate is precipitated by the action of sulfuric acid on a methyl alcohol solution of calcium oxide[2] or by the addition of ethyl alcohol to an equal volume of a saturated solution of calcium sulfate.[3]

Like strontium sulfate (p. 58), calcium sulfate appears to form a positive colloid during the process of precipitation. From a given pair of precipitants, calcium sulfate is thrown down directly either as the dihydrate or as the hemihydrate, the determining condition being the temperature of precipitation.[4]

Colloidal behavior of calcium sulfate is encountered in the highly dispersed products plaster of Paris and the so-called "soluble anhydrite" formed by the dehydration of the dihydrate under suitable conditions. These substances possess hydraulic properties, reacting with water and setting to form a coherent mass.

The System Calcium Sulfate-Water

The Existence of Calcium Sulfate Hemihydrate

Calcium sulfate is ordinarily believed to exist in three chemical forms, the dihydrate $CaSO_4 \cdot 2H_2O$; the hemihydrate $CaSO_4 \cdot 0.5H_2O$, commonly called plaster of Paris; and the anhydrous salt. Two crystalline modifications of the anhydrous salt have been identified by x-ray diffraction analysis. One form obtained by igniting gypsum fairly strongly gives the same orthorhombic pattern as the mineral anhydrite. Since neither the synthetic product nor the mineral possesses hydraulic properties, this form is commonly called insoluble anhydrite. A second crystalline form, hexagonal, obtained by igniting gypsum or hemihydrate between 100 and 200°, possesses

[1] Von Weimarn: Repts. Ind. Research Inst., Osaka, Japan, **12**, 117 (1931).
[2] Neuberg: Sitzber. preuss. Akad. Wiss., 820 (1907).
[3] Cavazzi: Kolloid-Z., **12**, 196 (1913).
[4] Lambert and Schaffer: J. Chem. Soc., 2648 (1926).

hydraulic properties and was called by van't Hoff [5] soluble anhydrite. Since both the hexagonal and the orthorhombic forms can apparently be obtained in both the hydraulic and non-hydraulic state, the terms soluble anhydrite and insoluble anhydrite are misnomers. Balarew [6] and Ramsdell and Partridge [7] have suggested that the product formed by dehydrating hemihydrate be called "dehydrated hemihydrate" to distinguish it from the orthorhombic anhydrite. This terminology will be used in this chapter.

Although calcium sulfate hemihydrate or plaster of Paris is generally included among the time-honored compounds, several papers have appeared in recent years which question the individuality of hemihydrate and the mechanism of its dehydration. Linck and Jung [8] deduced from dehydration data that plaster of Paris loses its water after the manner of zeolites. Balarew,[9] at different times, has been on all sides of the question. At first he claimed that the dehydration isobar would indicate the water to be present in the form of a true hydrate; later he stated that the dehydration curves show the water to be held in a new way "half-hydratic and half-zeolitic"; finally he concluded that the water is lost in the manner of zeolites. Gibson and Holt [10] concluded from temperature-pressure curves that the water is lost continuously as in a zeolite. Parsons [11] claimed that all the water in gypsum may be lost by heating without the intermediate formation of a hemihydrate.

Jung,[12] Ramsdell and Partridge,[13] and Caspari [14,15] reported that the x-ray diffraction patterns of calcium sulfate hemihydrate and its dehydration product are identical, in agreement with the view that the hemihydrate is a zeolite. Onorato [16] and Gallitelli [17] found the

[5] Van't Hoff, Armstrong, Hinrichsen, Weigert, and Just: Z. physik. Chem., **45**, 257 (1903).

[6] Kolloid-Z., **48**, 63 (1929).

[7] Am. Mineral., **14**, 59 (1929).

[8] Z anorg Chem., **137**, 407 (1924); *cf.* Krauss and Jorns: Tonind-Ztg., **54**, 1467, 1483 (1930).

[9] Z. anorg. Chem, **156**, 258 (1926); Kolloid-Z., **48**, 63 (1929); Balarew and Koluschewa: **70**, 288 (1935).

[10] J. Chem. Soc., 638 (1933).

[11] Univ. Toronto Studies, Geol. Ser., No. 24, p 24 (1927).

[12] Z. anorg. Chem., **142**, 73 (1925).

[13] Am. Mineral., **14**, 59 (1929); *cf., also,* Partridge and White: J. Am Chem. Soc, **51**, 360 (1929).

[14] Nature, **133**, 648 (1934).

[15] Proc. Roy. Soc. (London), **155A**, 41 (1936).

[16] Periodico mineral. (Rome), **3**, 138 (1932).

[17] Periodico mineral. (Rome), **4**, 1, 132 (1933).

hemihydrate and dehydrated hemihydrate to have the same type of structure but recognized minor differences in the powder diagrams. Feitknecht [18] likewise observed small differences in the two patterns provided care was taken to prevent rehydration of the dehydrated product, a precaution that Jung apparently overlooked.

Although the evidence cited above indicates that calcium sulfate hemihydrate is not a true hydrate, dehydration and x-ray studies carried out in the author's laboratory [19] lend strong support to the view

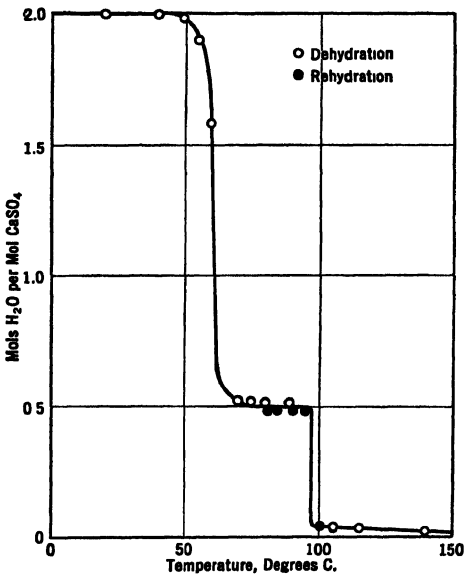


FIG. 8.—Isobaric dehydration curve for $CaSO_4 \cdot 2H_2O$.

that the hemihydrate is a definite chemical individual and that the process of dehydration is not zeolitic in character.

Isobaric Dehydration. Pure transparent selenite $CaSO_4 \cdot 2H_2O$ was subjected to isobaric dehydration (vapor pressure 23.6 mm) taking special care to secure equilibrium at each temperature by holding the sample for days or weeks, weighing at intervals until a constant state was attained. The results for both dehydration and rehydration are shown graphically in Fig. 8. The hemihydrate portion of the

[18] Helv. Chim. Acta, **14**, 85 (1931).

[19] Weiser, Milligan, and Ekholm: J. Am. Chem. Soc., **58**, 1261 (1936).

curve is enlarged in Fig. 9. The points on the curves represent the average of four values which differ by not more than 0.006 mol of water per mol of calcium sulfate. The dehydration isobars for the hemihydrate are typical for a definite hydrate which adsorbs a small amount of water and gives a dehydration product which likewise adsorbs water. Since the hemihydrate and especially the dehydrated hemihydrate are known to adsorb water, the evidence seems conclusive that when $CaSO_4 \cdot 2H_2O$ is dehydrated isobarically a definite hydrate $CaSO_4 \cdot 0.5H_2O$ which adsorbs a small amount of water is

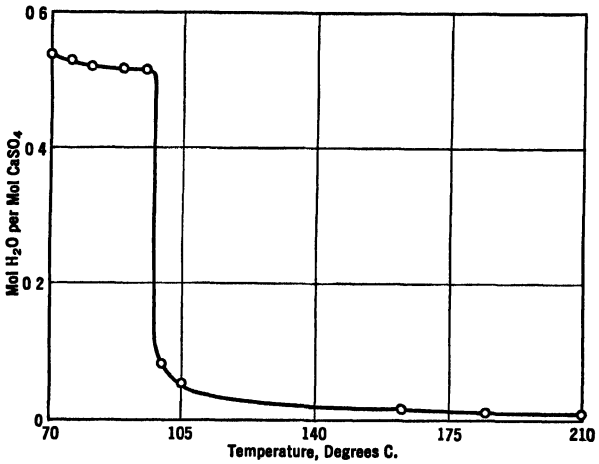


FIG. 9.—Isobaric dehydration curve for $CaSO_4 \cdot 0.5H_2O$.

first formed and this in turn dehydrates in stepwise fashion to dehydrated hemihydrate, $CaSO_4$, which adsorbs water that is not removed completely at a vapor pressure of 23.6 mm until well above the decomposition temperature. The dehydration is reversible, but there is no indication that the water is present in the zeolitic form unless one wishes to apply the term "zeolitic" to the very small amount of water adsorbed first by the very finely divided hemihydrate and later by the resulting dehydrated hemihydrate. The transition temperature of minute crystals of hemihydrate $\rightleftarrows$ dehydrated hemihydrate is approximately 97° [20] at 23 mm; and 107° at 971 mm. Nacken and Fill [21] claim that "soluble anhydrite" is formed at 20° in dry air or

[20] *Cf.* Balarew: Z. anorg. Chem., **156**, 258 (1926); **163**, 137 (1927).
[21] Tonind.-Ztg., **55**, 1194 (1931); *cf.* Krauss: **55**, 1222 (1931).

in a vacuum. From solubility studies Partridge and White [22] found the transition temperature of gypsum to hemihydrate to be 98° and from gypsum to anhydrite to be slightly below 40°, both in contact with water. In accord with van't Hoff, plaster of Paris goes over slowly to dehydrated hemihydrate in contact with water at 100°.

X-ray Examination. In the light of the dehydration experiments, one would expect the x-ray diffraction pattern for the hemihydrate to differ somewhat from that of its dehydration product. This was found to be true by comparing the patterns obtained with a Seemann crystal analysis apparatus using $K_\alpha Cu$ radiation and a precision Debye-Scheerer camera. The films were calibrated by mixing a small amount of pure nickelous oxide with the samples examined. The x-ray diffraction data are represented diagrammatically in Fig. 10. It is ap-

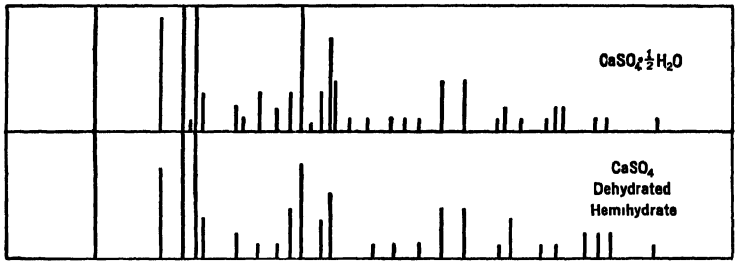


FIG. 10.—Diagrams of the x-ray diffraction patterns of $CaSO_4\ 0.5H_2O$ and $CaSO_4$ (dehydrated hemihydrate).

parent that the patterns of the two substances are similar, showing that the structures are similar; but the existence of definite differences between the two indicates that the water molecules in the hemihydrate occupy fixed positions in the lattice.

Caspari [15] failed to observe the small but significant differences on comparing x-ray rotation diagrams of large crystals of the two substances; but he demonstrated conclusively that the crystals possess a hexagonal structure. Weiser and Milligan [23] found the same characteristic differences in the powder diagrams of macrocrystals that they observed with microcrystals. Moreover, the dehydration isobar for the macrocrystals was a step-curve like that in Fig. 9.

The crystal structure of gypsum is monoclinic. Davis [24] postu-

[22] J. Am. Chem Soc., **51**, 360 (1929); Toriumi and Hara: J. Chem. Soc., Japan, **55**, 1051 (1934).

[23] J. Am. Chem. Soc., **59**, 1456 (1937).

[24] J. Soc. Chem. Ind., **26**, 727 (1907).

lated an unstable rhombic modification, but this has not been disclosed by x-ray diffraction studies. Rohland[25] assumed the existence of three anhydrous forms of calcium sulfate in addition to dehydrated hemihydrate and anhydrite; but here, also, x-ray analysis has failed to establish the identity of the alleged modifications. It appears therefore, that four and only four crystalline modifications of calcium sulfate have been identified: the dihydrate, monoclinic; the hemihydrate, hexagonal; dehydrated hemihydrate, hexagonal; and anhydrite, orthorhombic.

The Formation of Hydraulic Plasters. The most common gypsum plasters are plaster of Paris and dehydrated hemihydrate. By referring to Fig. 8 it will be seen that gypsum may be burned to plaster of Paris at as low a temperature as 65° at 23 mm vapor pressure; but the time required under these conditions is excessive. From a survey of the literature[26] it appears that, in technical practice, the gypsum is burned at temperatures varying from 120 to 200° in either a kettle or rotating kiln using coal, gas, or electric heat.[27] Since gypsum loses water more readily at 200° than at 120°, the heating must be shorter at the former temperature to burn to the same end point, provided the kilns are otherwise the same. This was demonstrated experimentally by Keane[26] and is substantiated by Hursch's[26] statement: "Commercially temperatures up to 200° or above are used but for short periods of time." The best temperature for commercial burning varies with the cost of fuel, the size and nature of the plant, etc.

Since the inversion temperature for plaster of Paris-dehydrated hemihydrate is 97° at 23 mm, it is probable that the original plaster contains more or less of the completely dehydrated product, especially when the burning temperature is high. But if the plaster is allowed to stand in moist air for a time, the dehydrated hemihydrate hydrates completely to plaster of Paris.

If the ignition is carried out for too long a time above 200°, anhydrite is formed which hydrates very slowly[28] and is known as dead-

[25] Z. anorg. Chem., **31**, 437 (1902); **35**, 194; **36**, 332 (1903); *cf.* Lacroix: Compt. rend, **126**, 360, 553 (1898); Gaubert: **197**, 72 (1933); Bull. soc. franc. mineral., **57**, 252 (1934).

[26] *Cf.* Keane: J. Phys. Chem., **20**, 701 (1916); Rogers: "Manual of Industrial Chemistry," 5th ed., **1**, 374 (1931); Read: "Industrial Chemistry," 232 (1933); Hursch: Trans. Am. Ceram. Soc., **17**, 549 (1915).

[27] Tupholme: Ind. Eng. Chem., News Ed., **13**, 441 (1935).

[28] *Cf.* Chassevent: Compt. rend., **194**, 786 (1932); *cf.* Stratta: Industria chimica, **9**, 28 (1934).

burned plaster. Jolibois [29] gives about 365° as the point above which dead-burned plaster results. But at higher temperatures between 600 and 1000°, a plaster known as flooring plaster or Estrich gypsum is formed. This sets more slowly than plaster of Paris but gives a very hard and highly resistant plaster. A product known as Keene's cement is made by burning the gypsum at red heat, cooling it, impregnating it with an alum solution, and igniting once more. The trace of alumina is said to catalyze the setting process, but since plaster formed at red heat will set without its presence, the action of alumina is not known with certainty.

It is apparently necessary to use temperatures above 500° in preparing flooring plasters, but this is probably determined in part by the time of ignition. Muller says that a temperature of 800–900° is best, and Glasenapp [30] recommends 900° although temperatures from 800–1300° give a satisfactory product.

Since gypsum ignited below 200° sets readily and that ignited around 300–400° sets very slowly if at all, one might attribute the difference primarily to crystal structure, the setting compound being hexagonal dehydrated hemihydrate and the non-setting compound being orthorhombic anhydrite. Although this is a factor, it is probably not the most important one. Thus, one can prepare dehydrated hemihydrate which will not set at a little above 30° in contact with a solution of sodium chloride,[5] and anhydrite which will set is prepared at 800 to 1000°. The difference in the setting power of different samples of dehydrated hemihydrate on the one hand, and anhydrite on the other, is probably due in large measure to the size and physical character of the particles of the respective preparations.[31] In support of this view, Keane [32] showed that gypsum calcined at 600° behaved like dead-burned plaster when the particles were 0.05 mm in diameter but set quite rapidly to a hard resistant mass when the particle size was reduced by grinding to 0.005 mm in diameter. Gill [33] found that both finely ground anhydrite and rough lumps of dead-burned plaster were bound firmly together by gypsum crystals after

[29] Bull. soc. chim., (4) **41**, 117 (1927).

[30] Z. angew. Chem., **27** III, 308 (1914); Tonind.-Ztg., **32**, 1148, 1197, 1230 (1908).

[31] *Cf.* Desch: Trans. Am. Ceram. Soc., **18**, 15 (1918-19).

[32] J. Phys. Chem., **20**, 701 (1916); Winterbottom: Bull. S. Australian Dept. Chem., 7 (1917).

[33] J. Am. Ceram. Soc., **1**, 65 (1918).

standing covered with water for 6 years; and Hartner[34] confirmed Keane's observation that natural anhydrite sets if ground to an extremely fine powder. Since anhydrite is 1.5 times as soluble as gypsum, setting of anhydrite will take place if the particle size is reduced to the point where the rate of solution and hydration is high enough to give a supersaturated solution of gypsum. Electrolytes which increase the solubility and rate of solution may be added to make the anhydrite set.[35]

The effect of particle size on the rate of solution of anhydrite has been studied in detail by Roller.[36] Some data are shown graphically

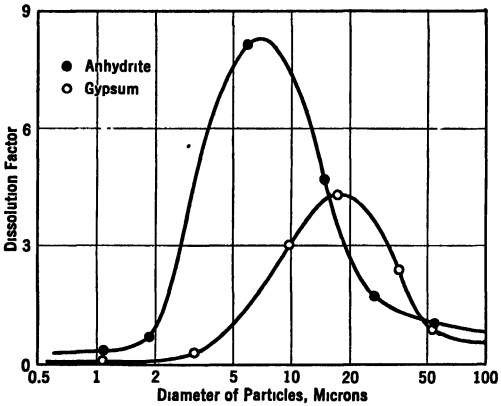


FIG. 11.—Effect of particle size on the rate of solution of anhydrite and gypsum.

in Fig. 11, in which the particle size is plotted against the dissolution factor, which is the relative specific rate of solution of each fraction referred to some fraction, usually the coarsest, taken as unity. Two procedures were followed, one in which the anhydrite powder was added dry to the water, and the second in which the powder was first dispersed with a small amount of water. All conditions of a given series of experiments were maintained constant except the particle size. It will be seen that for the powder added dry the maximum dissolution factor is at 8μ. Moreover, the dissolution factor is ap-

[34] Z. angew. Chem., **33** I, 175 (1920); Weissenberger: Kolloid-Z, **32**, 181 (1923).

[35] Budnikov: Compt. rend., **183**, 387 (1926); Z. anorg. Chem., **155**, 141 (1926); Sexton: Can. Mining J., **51**, 247 (1930).

[36] J. Phys. Chem., **35**, 1133 (1931); **36**, 1202 (1932).

proximately the same with the dispersed and dry anhydrite for a fraction in which the mean diameter of the particles is 26.5μ. For smaller particles it is less for the dispersed powder, until a flat inflection point is reached that lies near the particle size corresponding to the maximum for the powder added dry, that is at 8μ. At the inflection point the rate of solution is, by definition of the solution factor, strictly proportional to the surface exposed. With further decrease in particle size beyond the inflection point, the dissolution factor of the dispersed powder increases continuously.

The observed behavior is interpreted in the light of the theory that solution takes place from active centers which involve the edges and corners of a crystal. For the dry powder, the rate of solution is determined by the structure of the sediment. For the initially dispersed anhydrite, the same situation holds for particles larger than 8μ. Between 8μ and 50μ the enhanced rate of solution results from increasing dispersity of the anhydrite; with decrease in particle size to 8μ, the physical interaction of the grains vanishes and the rate of solution is proportional to the exposed surface. Below 8μ, the increasing rate with diminishing particle size is attributed solely to the effect of edges and corners.

Because of the observed effects of size and physical nature of particles on the rate of solution of anhydrite, it is not immediately obvious why one gets a non-setting plaster by burning at 300–400° and a setting plaster by burning at 800–900°. Other things being equal one would expect to get larger, more perfect, and more slowly soluble crystals at the higher temperature, in opposition to the facts. A logical interpretation of this behavior would be that an allotropic modification of anhydrite is formed at the higher temperature; but this is not so. It has been suggested that Estrich gypsum or flooring plaster is basic sulfate resulting from the decomposition of the anhydrite;[37] but this seems to be open to question first because the existence of a basic sulfate has not been established and second because anhydrite decomposes only slightly below 1000°.[38] It is possible, however, that the decomposition is sufficient to cause some cracking or shattering of the crystals which would increase the number of corners and edges and thus hasten the rate of solution.

[37] Glasenapp: Tonind.-Ztg., **32**, 1148, 1197, 1230 (1908); Grengg: Z. anorg. Chem., **90**, 327 (1914); Gallo: Gazz. chim. ital., **44** I, 497 (1914).

[38] Budnikov and Syrkin: Chem.-Ztg., **47**, 22 (1923); *cf.* Cobb: J. Soc. Chem. Ind., **29**, 69 (1910).

The Mechanism of the Setting of Plaster of Paris

The setting of plaster of Paris involves a definite chemical transformation from the hemihydrate to the dihydrate of calcium sulfate. Since the hemihydrate is 4.5 times as soluble as the dihydrate [39] at room temperature, Le Chatelier [40] assumed the following mechanism for the setting process: The hemihydrate first forms a saturated solution in water, then reacts to form the dihydrate giving a supersaturated solution from which is deposited a compact mass of interlacing needle-shaped crystals—the set plaster.[41] The amount of water necessary to bring the hemihydrate back to the fully hydrated condition is much less than is necessary to dissolve it since a given amount of solution supersaturated with respect to gypsum deposits crystals, thereby releasing the water to dissolve another portion of hemihydrate—the process continuing until the transformation to gypsum is complete.

For more than a quarter of a century Le Chatelier's theory of the mechanism of the setting of plaster of Paris was regarded as completely satisfactory. But in more recent years, it has been considered by a number of investigators as inadequate to account for all the facts. Following the lead of W. Michaelis [42] and Keisermann,[43] who observed the formation of a jelly as well as of crystals in the setting of Portland cement (p. 435), they have visualized the formation of some kind of a jelly as an intermediate stage in the setting of plaster of Paris. Thus, Cavazzi [44] observed that gypsum precipitated rapidly from aqueous solution with alcohol gave a gelatinous mass from which distinct crystals separated on standing. Without further evidence, he concluded that there was probably an intermediate gel stage in the setting of plaster.

Traube [45] was the next to suggest that colloidal behavior plays a rôle in the setting process. It is a well-known fact that soluble salts may have a marked effect on the setting rate,[46] some salts accelerating

[39] Marignac: Ann. chim. phys., (5) **1**, 274 (1874).

[40] "Recherches expérimentales sur la constitution des mortières hydraliques," Paris (1887); *cf., also,* van't Hoff *et al:* Z. physik. Chem., **45**, 257 (1903); Rohland: Z. anorg. Chem., **31**, 437 (1902); **35**, 194; **36**, 332 (1903); Jolibois and Chassevent: Compt. rend, **177**, 113 (1923).

[41] *Cf., also,* Chassevent: Ann. chim., **6**, 244, 313 (1926); **7**, 43 (1927).

[42] Chem.-Ztg., **17**, 982 (1893); Kolloid-Z., **5**, 9 (1909); **7**, 320 (1910).

[43] Kolloid-Beihefte, **1**, 423 (1910).

[44] Kolloid-Z., **12**, 196 (1913); *cf.* Neuberg and Rewald: **2**, 354 (1908).

[45] Kolloid-Z., **25**, 62 (1919).

[46] Ditte: Compt. rend., **126**, 694 (1898).

it and others retarding it. To account for this behavior Rohland [47] assumed, in accord with Le Chatelier's theory, that any salt which increases the solubility of calcium sulfate will accelerate the setting whereas any salt which decreases the solubility will retard the setting. This explanation is inadequate since small amounts of soluble sulfates decrease the solubility of gypsum and yet increase the rate of set. And there are other exceptions.[48] Traube observed the effect of salts on the time required for the plaster to attain a definite state of hardness. He found cations to be especially important, the order of influence being the reverse of that in which they precipitate sols. This led him to the conclusion, which is not obvious, that some kind of colloidal behavior must be involved in the setting process.

Ostwald and Wolski [49] likewise concluded from indirect evidence that colloidal processes are probably involved in the setting of plaster of Paris. Experimentally, they followed the rate of change in viscosity of suspensions of plaster, varying the concentration of the suspensions, the degree of dispersion, the temperature and the nature of the medium, *i.e.*, using solutions of various salts as well as pure water. The theoretical deductions from the experimental data were promised in a second paper which was never published. They merely state that the viscosity data indicate a colloid process, "as for example, the separation of perhaps only a thin gel layer as an integral part of the setting process."

The guarded statement of Ostwald and Wolski that "perhaps only a thin gel layer" was formed at some stage of the setting process, together with their failure to discuss theoretically their viscosity data, suggests that they were probably in doubt as to whether there was any gel formation at all. In marked contrast, Baykov,[50] Neville,[51] and Budnikov [52] came out definitely in support of the formation of a gel as an intermediate stage in the setting process. Baykov reached this conclusion as a result of a procedure which he claimed would give a gypsum jelly. Five to ten grams of hemihydrate were mixed with 100 cc of water or 10% $(NH_4)_2SO_4$ solution and shaken vigorously. On stopping the shaking after a suitable time, the entire mass was

[47] Z. Elektrochem, **14**, 421 (1908).

[48] Haddon: J. Soc. Chem. Ind., **39**, 165*T* (1920); **40**, 122*T* (1921); *cf.* Welch: J. Am. Ceram. Soc., **6**, 1197 (1923).

[49] Kolloid-Z., **27**, 79 (1920); Neugebauer: **31**, 40 (1922).

[52] Kolloid-Z., **42**, 151 (1927); **44**, 242 (1928).

[50] Compt. rend., **182**, 129 (1926); *cf.* Budnikov: Kolloid-Z., **42**, 151 (1927).

[51] J. Phys. Chem., **30**, 1037 (1926).

said to set to a "gelatinous mass presenting the appearance of a silica gel." Weiser and Moreland [53] showed that this precedure did not give a true gel but a network of relatively long crystal needles of gypsum. The only resemblance between this cloudy, non-uniform entangling mass of crystal needles and silica gel was that both stayed in an inverted beaker.

Since the hydration of plaster of Paris is an exothermic reaction, the rate of the reaction may be followed by measuring the rate of evolution of heat. This has been done by Cloez,[54] Emley,[55] Chassevent,[56] Neville,[57] Budnikov,[58] Hansen,[59] and others. Starting with a high grade of hemihydrate mixed with pure water and determining the rise in temperature with time, an S-shaped curve is obtained. For an interval of several minutes the temperature rises but slightly, after which it goes up relatively rapidly to a maximum, and then falls off. Neville observed that a so-called "initial set," [60] results before there is any marked heat evolution. He concluded from this that the setting takes place in two stages: (1) the formation of a gel or adsorption complex between the plaster and water, a process accompanied by but little heat effect; and (2) the exothermic reaction between the plaster and the adsorbed water, forming gypsum. At first he attributed the observed contraction in volume to the initial step and the subsequent expansion to the second step, but later [61] he concluded that the hydration which causes the initial contraction takes place throughout the whole period but is masked for a time by the thermal expansion.[62] The action of salts on the rate of setting was attributed to their effect on the adsorption of water to form a gel and subsequently to their catalytic action on the reaction between hemihydrate and water.

Budnikov carried out thermometric observations on the rate of setting of plaster under varying conditions, apparently quite independently of the work of Neville, and reached similar conclusions as to the mechanism of the process. There is a distinct difference in

[53] J. Phys. Chem., **36**, 1 (1932); Colloid Symposium Monograph, **9**, 1 (1931).
[54] Bull. soc. chim., (3) **29**, 171 (1903).
[55] Trans. Am. Ceram. Soc., **19**, 573 (1917).
[56] Ann. chim., **6**, 264 (1926).
[57] J. Phys. Chem., **30**, 1037 (1926); *cf., also,* Neville and Jones: Colloid Symposium Monograph, **6**, 309 (1928).
[58] Kolloid-Z., **44**, 242 (1928); Z. angew. Chem., **40**, 408 (1927).
[59] Ind. Eng. Chem., **22**, 611 (1930).
[60] *Cf., however,* Emley: Trans. Am. Ceram. Soc., **19**, 573 (1917).
[61] Neville and Jones: Colloid Symposium Monograph, **6**, 309 (1928).
[62] *Cf.* Williams and Westendick: J. Am. Ceram. Soc., **12**, 381 (1929).

the form of Neville's time-temperature curves and those obtained by Budnikov, who, apparently without knowing it, used a plaster containing a large amount of soluble anhydrite. Accordingly, there was a marked rise in temperature at the outset as a result of the hydration of the anhydrite to hemihydrate.[54,63] Budnikov goes a step further than Neville and postulates the formation of a gel around the plaster particles which protects them from the action of water, thereby producing the induction period which varies in length depending on the nature of the addition agents present. The period of induction is assumed to be broken by crystallization of the enclosing gel which allows the water to act again on the plaster. This theory deserves little consideration, for, if the facts are as postulated, the disappearance of the first gel layer would merely be followed by the formation of a new one giving a second induction period, and so on, the process being repeated indefinitely.

The arguments for gel formation as a step in the setting of plaster of Paris may seem quite conclusive if taken collectively. On reflection it appears, however, that all the evidence of true gel formation is indirect. No one has really observed the formation of a gel of gypsum prior to the appearance of the interlacing crystals in the plaster pastes. Chassevent,[56] independently of Neville or Budnikov, observed an initial inhibition period in the time-heat curves for the hydration of hemihydrate. It probably never occurred to him to invoke the formation of a gelatinous adsorption complex to account for this period of inhibition since he had previously observed an inhibition period in the crystallization of gypsum from its supersaturated solution in the absence of nuclei. Indeed, he found that solutions of gypsum containing five times the saturation value did not start to crystallize for 28 minutes when particular care was taken to exclude nuclei. The effect of salts on the rate of setting was also observed; he states that with potassium sulfate this "accelerates the crystallization and diminishes the time interval during which the instable saturated solutions of hemihydrate remain without crystallization."

Hansen[59] likewise failed to find any direct evidence of gel formation and, independently of Chassevent, reached the same conclusion: "the effect of foreign material upon the rate of precipitation from its supersaturated solution appears to explain the ability of foreign materials to accelerate or retard the setting of calcined gypsum pastes."

Although one can offer no objections to the statements of either Chassevent or Hansen, their conclusion in the last analysis is merely

[63] Chassevent: Ann. chim., 6, 265 (1926).

that foreign substances affect the rate of set by influencing the rate at which gypsum precipitates from its supersaturated solution. On the other hand, they offer no explanation of the variation in behavior with various substances. This will be considered in the following sections.

Effect of Gypsum Nuclei on the Rate of Set

It is a well-known fact that samples of high-grade plaster of Paris, free from any added accelerators or retarders, show considerable variation in the time of set. In general a plaster which exhibits a long period of inhibition before any marked rise in temperature takes place is designated a slow-setting plaster, whereas one with a short period of inhibition is referred to as a rapid-setting plaster. If the period of inhibition is caused by the building up of an adsorption complex "whereby the two reactants are brought into chemical contact," as Neville assumes, then it is not obvious why different samples prepared by similar procedures and having the same average particle size should show such differences in the period of inhibition. On the other hand, if the inhibition period is merely a phenomenon of supersaturation, the variation in the length of the period with different samples of plaster might well be caused by variation in the number of gypsum nuclei in the samples. Chassevent [64] showed that the addition of gypsum to plaster hastened the time of set, and Hansen [59] found that the time of setting was appreciably shortened [65] if a plaster paste was made with water shaken for 35 minutes with a small amount of plaster which ordinarily attained its maximum temperature in 75 minutes. But the importance of the presence of gypsum nuclei in plaster of Paris on the rate at which it sets has been pretty generally overlooked, especially by everybody who has visualized gel formation as a stage in the setting process.

To determine the effect of gypsum nuclei on the rate of set, Weiser and Moreland [58] added varying amounts of a standard sample of gypsum to a fixed amount of plaster of Paris and determined the setting time by the thermometric method, using a Dewar flask calorimeter. The "standard sample" was a high-grade commercial product previously heated for 2 hours at 130° and subsequently allowed to stand in a moist atmosphere to transform into hemihydrate the dehydrated hemihydrate formed during ignition. The time-temperature curves for various mixtures as given in Table VIII are shown in Fig. 12.

[64] Ann. chim., **6**, 313 (1926).

[65] *Cf.* Wiggin's Sons Co.: Brit. Pat. 221,853 (1923).

TABLE VIII

EFFECT OF GYPSUM NUCLEI ON THE RATE OF SET OF PLASTER OF PARIS

Substances mixed with 35 cc water			Time to attain maximum temperature, minutes
Plaster of Paris 50 g	Grams gypsum		
	Added	Calculated	
Sample heated 5 hours	0 0	0 00012	100 0
Standard sample	0.0	0 00092	64 0
" "	0.01	0 0098	38.0
" "	0.05	0.052	26.5
" "	0 10	0 08	24.0
" "	0.25	0.23	19.0
" "	0.50	0 50	16 0
" "	1 00	0.94	14.0

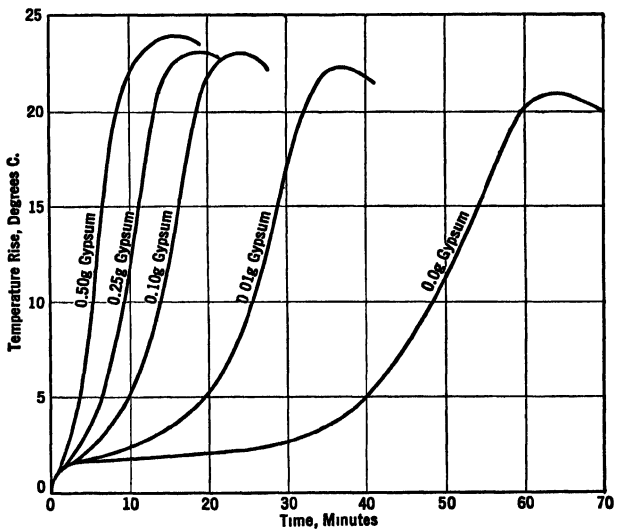


FIG. 12.—Time-temperature curves obtained with plaster of Paris seeded with varying amounts of gypsum.

From the form of the curve with a plaster to which no gypsum was added, it will be noted that at first the temperature rises abruptly

approximately 1°, probably as a result of the heat of wetting and of the transformation of a small amount of dehydrated hemihydrate into hemihydrate. The initial rise is followed by a "period of inhibition" after which there is a gradual increase in rate of reaction until a maximum temperature is attained. The sample heated for 5 hours (curve not shown) which was quite free from nuclei, did not attain the maximum temperature for 100 minutes, whereas the standard sample showed a shorter inhibition period and reached the maximum temperature in 65 minutes. The inhibition period was appreciably cut down by adding nuclei of gypsum until, with 0.5 g in 50 g of plaster, it was practically zero. When the time to attain the maximum temperature is plotted against the weight of gypsum nuclei added, a parabolic curve is obtained, which shows that the rate of set approaches infinity as the number of nuclei present approaches zero. For the particular experimental conditions, the curve is represented by the equation $W = 1.52 \times 10^5\ t^{-4.55}$, where W is grams gypsum added and t is time to attain maximum temperature. Using this equation, calculated values were obtained for the amount of gypsum present in the samples referred to in Table VIII.

The above observations indicate that the length of the inhibition period is influenced to a marked degree by the amount of gypsum nuclei in the plaster paste after the mixing with water is complete. Hence the observed inhibition period appears to result from delayed precipitation from a supersaturated solution owing to dearth of nuclei rather than to the time necessary to form a gel or adsorption complex. This was confirmed by a series of observations which show the effect of stirring the plaster-water mixtures on the rate of set.

Effect of Electrolytes on the Rate of Setting

Since the setting of plaster of Paris involves the precipitation of gypsum from its supersaturated solution, the effect of electrolytes may be considered in the light of von Weimarn's theory of the precipitation process. It will be recalled that the initial velocity of precipitation is proportional to the percentage supersaturation, $W = (Q - L)/L = P/L$, where Q is the total quantity of substance that is to precipitate and L is the solubility (p. 21). The solubility of plaster of Paris in water is approximately 0.067 mol/l, and when this hydrates to gypsum which has a solubility of but 0.015 mol/l, the percentage supersaturation is $(0.067 - 0.015)/0.015 = 3.5 = U$. The initial velocity of precipitation is proportional to U, that is, $W = K\ 3.5$. In view of the

relatively long period of inhibition following the mixing of pure plaster of Paris with water, it is obvous that this percentage supersaturation is insufficient to cause rapid precipitation of nuclei which must be present in abundance for a rapid reaction to take place throughout the mass. Now, if the addition of a foreign electrolyte cuts down the period of inhibition, it follows that the percentage supersaturation of the solution with respect to gypsum must be greatly increased. This may be accomplished in one of two ways: either the solubility of the hemihydrate is increased appreciably more than that of gypsum by the presence of the foreign electrolyte, or the solubility of the gypsum is decreased appreciably more than that of hemihydrate by the presence of the foreign electrolyte. In the first instance the value of $(Q - L)/L = P/L$, the percentage supersaturation, is increased because the value of Q, which is determined by the solubility of hemihydrate, is increased proportionately more than L, the solubility of the gypsum in the medium; and in the second, P/L is increased because L is decreased proportionately more than P in the given medium. In other words, for a foreign electrolyte to change the initial rate of formation of nuclei as compared to the rate of formation in water alone, all that is necessary, other things being equal, is for the ratio of the solubility of hemihydrate to the solubility of gypsum to be greater or less than 4.5, the ratio of the solubilities in pure water. There is, of course, no reason to expect a constant ratio of solubilities in widely different environments, but direct evidence of such variation in the solubility ratios is often quite impossible to get since solutions of foreign electrolytes added to hemihydrate usually result in such rapid precipitation of gypsum that the solubility of hemihydrate in the solution cannot be determined accurately. On the other hand, the observations recorded in the subsequent paragraphs furnish strong indirect evidence of the expected variation in the solubility and in one case this has been evaluated directly.

The rate of growth on nuclei already present is given by the Nernst-Noyes equation (p. 12), which states that the velocity of growth is proportional to $Q - L$, the absolute supersaturation. For a given amount Q in solution, the velocity of growth is influenced strongly by the solubility. If L is small so that $Q - L$ is relatively large, the growth of particles will be relatively rapid; whereas, if L is large so that $Q - L$ is relatively small, well-formed crystals will build up slowly. As is well known, for the growth of large well-formed crystals, the $Q - L$ value must be very small and few nuclei must be present on which precipitation takes place.

Effect of Ammonium Nitrate. Since ammonium nitrate is quite soluble and the solubility of gypsum in a wide range of concentration is known,[66] this salt will be used to illustrate the effect of electrolytes on the rate of set as measured by the time to attain maximum temperature. The results of a series of observations are shown graphically in Fig. 13. The same general procedure outlined above was followed, using the same plaster. It is apparent that, for concentrations

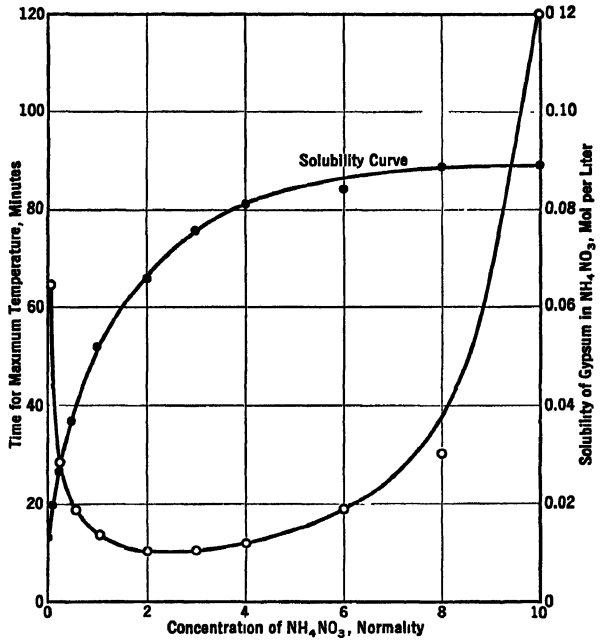


FIG. 13.—Effect of ammonium nitrate concentration on the rate of set of plaster of Paris.

of salt in the neighborhood of 1 to 2 *N*, the inhibition period is very small and the rate of set quite rapid; with concentrations below 1 *N*, the inhibition period and the time of set become gradually longer, approaching those of pure water. The same is true for higher concentrations as evidenced particularly by the behavior of 10 *N* solution where the inhibition period and time of set are much longer than in

[66] Cameron and Brown: J. Phys. Chem., **9**, 210 (1905).

pure water. The U-shaped form of the rate-of-set curve indicates that, at low concentrations of nitrate solution, the ratio of the solubility of hemihydrate to gypsum is sufficiently large that a high percentage supersaturation of gypsum obtains. This results in prompt precipitation of nuclei, and, because of relatively high absolute supersaturation, the reaction goes rapidly to completion. On the other hand, in strong nitrate solution in which gypsum is quite soluble, $Q - L = P$ is small and P/L is so small that the initial formation of nuclei and the subsequent growth of crystals are greatly retarded. This interpretation was confirmed in a striking way by comparing the size of crystals formed in nitrate solutions of different concentrations.

For a complete quantitative formulation of the rate of formation and the nature of the precipitate as it is affected by the solubility of the substances concerned, it would be necessary to know the solubility of plaster of Paris as well as of gypsum in varying concentrations of ammonium nitrate. At low concentrations of nitrate the rate of transformation of hemihydrate is too high to obtain such data; but in 10 N nitrate, the rate of transformation is sufficiently slow that the solubility of hemihydrate may be obtained fairly accurately. Weiser and Moreland [58] found the solubility in 10 N nitrate to be 0.114 mol/l as compared with 0.089 mol/l for the solubility of gypsum in the salt solution. The ratio of solubilities is thus 1.3 as compared with 4.5 in pure water, and $(Q - L)/L$ in the nitrate solution is 0.3 as compared with 3.5 in pure water. These data furnish a quantitative basis for the above explanation of the observed differences in behavior of plaster of Paris in different solutions.[67]

Effect of Various Salts. The effect of a number of electrolytes on the rate of set of plaster of Paris is shown graphically in Fig. 14. It will be noted that the curves are U-shaped,[68] except the one using ammonium acetate (see below). The similarity of the curve with ammonium sulfate to that with ammonium nitrate is especially interesting since the solubility curve of gypsum in ammonium sulfate passes through a minimum. This shows that the effect of a salt on the solubility of gypsum is altogether insufficient to explain its effect on the rate of set.[69] The important thing is the ratio of the solubility of plaster to that of gypsum in a concentration of salt, since this ratio determines the initial percentage supersaturation which influences greatly

[67] *Cf.* Yamane: Sci. Papers Inst. Phys. Chem Research (Tokyo), **18**, 101 (1932).

[68] *Cf., also,* Gibson and Johnson· J. Soc. Chem. Ind., **51**, 25*T* (1932).

[69] *Cf.* Neville: J. Phys. Chem., **30**, 1037 (1926).

the rate of formation of nuclei, and the absolute supersaturation which determines the rate of growth. The form of the ammonium sulfate curve indicates that the ratio of the solubility of plaster of Paris to gypsum is high even in relatively low concentrations of ammonium sulfate where the solubility of gypsum is less than in pure water.

X-radiograms of the crystals of widely different shapes obtained in the action of plaster of Paris in solutions of the several electrolytes

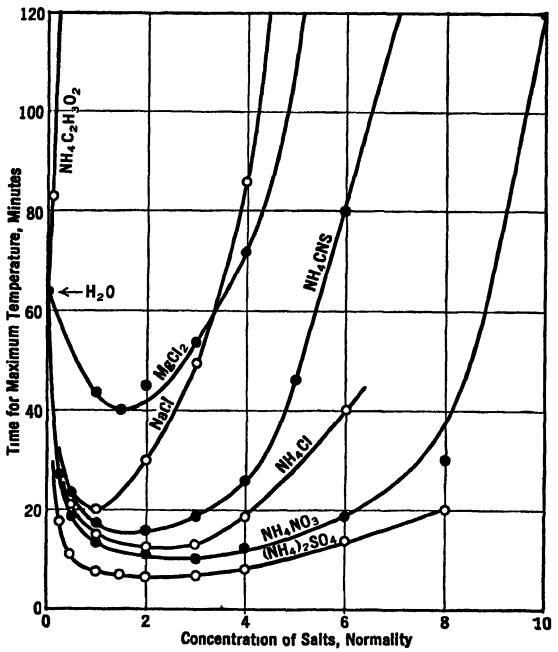


FIG 14.—Effect of varying concentrations of several electrolytes on the rate of set of plaster of Paris.

showed them to be identical in structure with gypsum formed in the presence of water alone.

Unlike the other salts included in Fig. 14, ammonium acetate exerts a marked retarding action on the rate of set. This would not be predicted from the von Weimarn theory since the rate is much slower than would be expected from solubility relations and the prevailing supersaturation. The reason for the retarding action was traced by

Weiser and Moreland [58] to the fact that gypsum does not deposit readily from its supersaturated solution on gypsum nuclei formed in the presence of ammonium acetate, probably because of an adsorbed film of acetate on the surface of the crystals. The addition of gypsum crystals formed in the absence of acetate, or of broken crystals formed in the presence of acetate, induces a rapid rate of set. Ammonium citrate and alkali borates and biborates [70] likewise exert a retarding action. It would appear that the action of such salts is similar to that of small amounts of glue and gelatin, the adsorption of which on gypsum nuclei inhibits or prevents the growth of the crystals [71] and so delays or prevents the setting of the plaster. It is said that the ancient Romans used blood to retard the rate of set of plaster of Paris.

Gibson and Johnson [70] found that borates even in low concentration reduced the expansion on setting of plaster of Paris. It was suggested that, by adjusting the proportion of potassium sulfate, an accelerator, and borax, a solution could be made up which would give any desired rate of set and a very low expansion. It thus appears that the rate of setting, linear expansion, hardness, and compressive strength may be controlled by the number of gypsum nuclei present, the plaster-water ratio, the time of mixing, the presence of soluble salts, and, to a limited extent, by the temperature.[72]

The utility of plaster of Paris in the preparation of casts depends on its power of filling the mold by the expansion on setting and so taking a sharp impression of its surfaces. Although there is an expansion, the final volume of the crystallized gypsum is less than the sum of the original volumes of the materials by about 7%, as can be calculated from the respective densities of the substances concerned.[73] The apparent density of a plaster cast is, however, less than that of the plaster and water constituting it, since the mass is porous, being made up of groups of interlocking crystals with spaces between them. The manner in which the crystals are laid down is probably the important factor in filling the mold. Borates reduce the normal expansion on setting by modifying the form of the interlocking crystals.

The initial contraction and subsequent expansion of plaster were well known in Persia, for up to about 1880 this property was utilized

[70] Gibson and Johnson: J Soc. Chim. Ind., **51**, 25*T*, 399*T* (1932).

[71] Ostwald and Wolski: Kolloid-Z., **27**, 78 (1920); Traube: **25**, 62 (1919); *cf.* Serb-Serbina and Dubinskii: J Phys. Chem., U.S.S.R, **5**, 1186, 1190 (1934).

[72] *Cf.* Johnson: Trans. Ceram. Soc., **32**, 284 (1933).

[73] Desch: "The Chemistry and Testing of Cement," 105, 108 (1911).

as a means of executing criminals.[74] The condemned individuals were placed in hollow stone columns and surrounded with wet plaster of Paris. At first they suffered but little inconvenience, but after a time they showed signs of distress and screamed loudly; finally, paralysis and death supervened. This doubtless occurred as the expansion of the plaster compressed the thorax and abdomen.

[74] *Cf.* J. Soc. Chem. Ind., **26**, 737 (1907).

CHAPTER V

THE COLLOIDAL CARBONATES, PHOSPHATES, CHROMATES, AND ARSENATES

COLLOIDAL CARBONATES

Formation of Gels and Sols

Neuberg[1] prepared sols of the carbonates of calcium, strontium, barium, and magnesium by conducting carbon dioxide into solutions of the oxides of the respective metals in methyl alcohol. For example, from a solution of barium oxide in the alcohol, carbon dioxide threw down a thick gel which was subsequently peptized, giving a transparent sol of the consistency of thick collodion. On concentrating the sol by evaporation in vacuum, it set to a jelly which was repeptized by shaking with methyl alcohol. Evaporation to dryness gave a transparent celluloid-like mass.

Buzágh[2] modified Neuberg's procedure by passing dry carbon dioxide for several hours into a suspension of the ignited oxides in methyl alcohol and filtering off the residue. The clear sol could be diluted with alcohol, ether, benzene, and chloroform without coagulation. Acetone and carbon disulfide gave flocculent precipitates, and a little water caused the sol to set to a jelly from which crystals of the metallic carbonate separated in a short time. The dispersed phase of the sols was found to be not the normal alkaline-earth carbonates but the dimethyl carbonates of the metals. The latter salts were obtained in a pure crystalline state by conducting carbon dioxide for several hours into methyl alcohol containing the finely divided oxides in suspension.

To prepare sols of the normal carbonates, Buzágh passed carbon dioxide into a suspension of the metallic hydroxides in methyl alcohol and filtered off the residue. The alcohols were converted to hydrosols by dialyzing against water. A more satisfactory method of preparing

[1] Neuberg and Neimann: Biochem. Z., **1**, 166 (1906); Neuberg and Rewald: Kolloid-Z., **2**, 321 (1908); Neuberg: Sitzber. preuss. Akad. Wiss., 820 (1907).
[2] Kolloid-Z., **38**, 222; **39**, 218 (1926).

the hydrosols consists in decomposing the dimethyl carbonates of the metals with a small amount of water. These sols contain, besides the insoluble alkaline-earth carbonate, some soluble bicarbonate and methyl alcohol which can be removed by dialysis.

Colloidal carbonates are readily prepared by the use of protecting colloids. Thus, colloidal carbonates of mercury,[3] lead,[3] and silver[4] are formed in the presence of the so-called protalbinates and lysalbinates of sodium; and colloidal calcium carbonate by precipitation in the presence of albumin, gelatin, and peptone.[5]

Constitution of Barium Carbonate Sol

Buzágh studied the constitution and properties of barium carbonate sol prepared by decomposition of the dimethyl carbonate. To prevent the sol from becoming basic, the dialysis was stopped before all the bicarbonate was removed. In order to make the barium and carbonate content exactly equivalent, sufficient barium hydroxide was added to convert into carbonate the bicarbonate which was known to be present from an analysis of the supernatant liquid after coagulating a sample of the sol. Even when the amounts of barium and carbonate were equivalent, the intermicellar liquid was found to contain bicarbonate ion from hydrolysis of carbonate: $CO_3^{--} + H_2O \rightleftarrows HCO_3^- + OH^-$. The constitution of the colloidal particles was deduced to be

$$\{(BaCO_3)_x[Ba(OH)_2]_n \cdot Ba_n^{++}\}^{2n+}$$

paired with $2nHCO_3^-$ ions. From the specific conductivity of a certain sol and its ultrafiltrate together with the mobilities of the colloidal particles and HCO_3^- ions and the concentration of $BaCO_3$, Ba^{++}, and HCO_3^-, it was calculated that, when $n = 1$, $x = 120$. The constitution of the particle was formulated $[120BaCO_3 \cdot Ba(OH)_2 \cdot Ba^{++}]^{++}$, associated with two HCO_3^- ions. The barium carbonate content of the particles was found to decrease with dilution and to increase with particle size, as one would expect.

Although the above method may give the number of single molecules in a colloidal particle, it would be well to have an independent confirmation by determining ultramicroscopically the number of particles in a given volume of a sol of known concentration. Since the barium carbonate sols contain particles of widely varying size, it is obvious that average values only will be obtained by either method.

[3] Leuze: "Zur Kenntnis kolloidaler Metalle und ihrer Verbindungen," 21, 28.
[4] Paal and Voss: Ber., **37**, 3862 (1904).
[5] Sabbatani and Salvioli: Atti ist. Veneto sci., Pt. 2, **71**, 1057 (1912).

There is no objection to expressing the supposed composition of a colloidal particle by a formula, but it should be recognized that colloidal particles, in general, are not complex ions of definite composition such as a cobalt amine cation or ferrocyanide anion. The barium carbonate particle is a finely divided portion of solid that adsorbs the bivalent barium ions more strongly than the univalent bicarbonate ions and so assumes a positive charge. The number of barium carbonate molecules in one of the solid particles will vary, of course, with the size and density of the particle which, in turn, are determined by the conditions of precipitation, the concentration, and the purity of the sol.

Coagulation of Barium Carbonate Sol

Barium carbonate sol is quite sensitive to the action of electrolytes. Since the particles show considerable variation in size, the sol may be

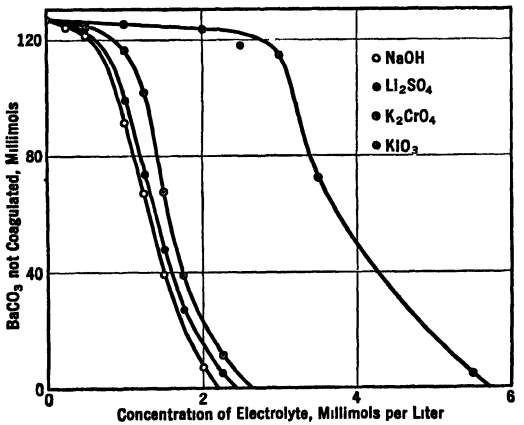


FIG. 15.—Fractional coagulation of barium carbonate sol by electrolytes.

precipitated fractionally by the stepwise addition of electrolytes, especially those with high precipitating power such as alkali hydroxide, sulfate, and iodate. It is claimed that alkali halides and nitrate which precipitate only in relatively high concentrations do not cause fractional coagulation. It is much more likely, however, that the fractional coagulation with the latter salts is less marked and so was overlooked. Some observations on the fractional coagulation of the sol are given in Fig. 15. To 5-cc portions of sol containing 25 g $BaCO_3$ per l was added 5 cc of electrolyte of varying concentrations. After standing 10 minutes, the mixture was centrifuged and the barium

content of the supernatant sol was determined. It will be seen that the order of precipitating power of the anions is: $OH > SO_4 > CrO_4 > IO_3$. As usual, iodate, which is taken to be a univalent ion, behaves more like a bivalent ion.[6]

The close relationship between particle size and fractional coagulation is illustrated by the observations given in Table IX.

TABLE IX

RELATION BETWEEN FRACTIONAL COAGULATION OF $BaCO_3$ AND PARTICLE SIZE

K_2SO_4 in millimol/l 5 cc added to 5 cc sol	$BaCO_3$, not coagulated	Average diameter of particles in the uncoagulated sol, mμ
0 0	147 2	198
0 2	143 0	178
0 4	128 0	148
0 6	73 0	89
0.8	28 0	77

COLLOIDAL PHOSPHATES

The slightly soluble orthophosphates of lead and the alkaline-earth metals are precipitated in a gelatinous form by the interaction of alkali phosphate and the metallic halides. Sols of these compounds have not been prepared in the absence of protecting colloids. De Toni[7] made sols of calcium orthophosphate by mixing hot solutions of sodium phosphate and calcium chloride in the presence of gelatin, gum arabic, blood serum, and starch. A sol is formed, also, by mixing dilute solutions of phosphoric acid and calcium hydroxide in the presence of gelatin. Hatschek[8] obtained rhythmic bands of calcium phosphate by allowing calcium chloride to diffuse into a gelatin gel containing normal sodium phosphate. Phosphate clays possessing the properties of typical colloidal gels have been described by Elschner.[9]

Colloidal silver orthophosphate is prepared by mixing 0.05 *N* solutions of $AgNO_3$ with a slight excess of 0.05 *N* Na_3PO_4 or

[6] *Cf* Weiser and Middleton: J. Phys. Chem., **24**, 51 (1920).
[7] Kolloid-Z., **28**, 145 (1921).
[8] Kolloid-Z., **27**, 225 (1920).
[9] Kolloid-Z., **31**, 94 (1922).

Na_2HPO_4.[10] The sol precipitates slowly on standing, but it may be stabilized by adding sodium "lysalbinate" or "protalbinate."[a]

Colloidal lead phosphate for use in cancer treatment[11] may be made by adding sodium phosphate solution drop by drop to a boiling solution of lead chloride containing gelatin, followed by centrifuging to remove any unpeptized material. The colloidally dispersed lead phosphate is said to be less toxic than lead acetate, colloidal lead, or colloidal lead oxide.[12]

COLLOIDAL CHROMATES

Colloidal Silver Chromate

Sols of silver chromate are formed by bringing together silver nitrate and potassium chromate in the presence of gelatin or sugar.[13] On mixing the solutions in the presence of gelatin, the resulting solution is yellow for a time and then turns red. The cause of this behavior has been the subject of several investigations and is still open to some question. Williams and MacKenzie,[14] Bolam and MacKenzie,[15] and Bolam and Donaldson[16] made electromotive force and conductivity measurements which show that, prior to the appearance of the red color, the activity of the silver ion in the yellow mixture is very much higher than in a pure saturated solution of silver chromate at the same temperature and that when the red color appears the activity of the silver ion decreases simultaneously to a marked degree. Desai and Nabar[17] found, further, from electrometric measurements that the activity of silver ion in the mixture remains constant for some minutes, then decreases rapidly, and finally becomes constant; and that the point at which the activity commences to fall corresponds in every instance to the appearance of the red color. The obvious conclusions from these observations is that the yellow mixture contains a highly supersaturated solution of silver chromate and that the red color is caused by the actual formation of the solid phase rather than by coagulation of a highly dispersed solid phase already present.

[10] Lottermoser: J. prakt. Chem., (2) **72**, 39 (1905).
[11] Bischoff and Blatherwick: J. Pharmacol., **31**, 361 (1927).
[12] *Cf.* Kehoe and Thamann: J. Lab. Clin. Med., **19**, 178 (1933).
[13] Lobry de Bruyn: Rec. trav. chim., **19**, 236 (1900); Ber, **35**, 3079 (1902).
[14] J. Chem. Soc., **117**, 844 (1920).
[15] Trans. Faraday Soc., **22**, 162 (1926); Bolam and Desai: **24**, 50 (1928).
[16] Trans. Faraday Soc., **29**, 864 (1933).
[17] Trans. Faraday Soc., **28**, 449 (1932); Nature, **127**, 628 (1931).

Dhar and collaborators,[18] on the other hand, made similar observations which indicate that two-thirds of the silver chromate is present in the colloidal state from the start. The yellow mixture was believed to be a sol in which the particles are negatively charged by adsorption of chromate ions, and the red a less stable sol, in which the particles are positively charged by adsorption of silver ions. Chatterji[19] failed to observe a decrease in the electromotive force with time. In accord with this, later work of Naik, Desai, and Desai[20] indicates that whatever changes take place in the conductivity of the mixture occur immediately on mixing the solutions and that there is no gradual decrease in conductivity with changes in the color of the mixtures. It was therefore concluded that the yellow mixtures contain some solid particles in a very highly dispersed condition, and that changes in color result from growth and agglomeration of very fine particles into larger ones.

These and other conflicting observations, both in different laboratories and in the same laboratory, may be due in part to differences in reagents, especially the gelatin, in the *p*H-value of the mixtures, and in the exact method of procedure. In this connection it has been found that hydrolyzed gelatin produces more highly dispersed silver chromate than unhydrolyzed gelatin.[21] It must be borne in mind, also, that the inhibiting action of gelatin may be quite complicated, involving one or more of the following: (1) prevention of the formation of crystallization centers, thereby producing a highly supersaturated solution; (2) prevention of growth of particles, thereby giving a system in which the particles may approach molecular dimension; and (3) prevention of agglomeration of particles. It is a mistake to assume that the inhibiting action gives rise to supersaturation only. By suitable adjustment of the temperature, amount of gelatin, *p*H of the gelatin, and concentration of the reactants Khanolkar, Barve, and Desai[22] found that the conductivity of the mixture (1) may not decrease at all while the color remains yellow, (2) may decrease some time after the color change, (3) may not change at all in spite of the color change.

[18] J. Phys. Chem., **28**, 41 (1924); Kolloid-Z., **54**, 270 (1924); J. Indian Chem. Soc., **5**, 175 (1928); Trans. Faraday Soc., **23**, 23 (1927).

[19] Proc. Indian Sci. Congr., 10 (1932).

[20] J. Indian Chem. Soc., **11**, 45; Desai and Naik: 59 (1934); J. Univ. Bombay, **2** II, 90 (1933).

[21] Bolam and Desai: Trans. Faraday Soc., **24**, 50 (1928); Ganguly: J. Indian Chem. Soc., **3**, 177 (1926).

[22] Proc. Indian Acad. Sci., **4A**, 468 (1936).

The behavior of silver and lead iodide in gelatin solutions is similar to that of silver chromate (p. 139).

The phenomenon of rhythmic precipitation was discovered in connection with silver chromate when Liesegang[23] placed a drop of silver nitrate on a glass plate coated with moist gelatin containing a small amount of potassium dichromate and obtained the series of rings now so well known. A similar experiment can be carried out in a test tube, giving the so-called rhythmic bands. Numerous investigations with silver chromate and many other substances have been carried out with the end in view of determining the mechanism of the banding process. The various theories have been considered elsewhere (Vol. II, pp. 24, 180) and will not be repeated here. The inhibiting action of gelatin on the precipitation of silver chromate must influence the ring formation in gelatin jelly. This, however, is of minor importance in a general theory of rhythmic banding since silver chromate will precipitate rhythmically under suitable conditions in the absence of a jelly.

Colloidal Lead Chromate

A lead chromate sol is formed by precipitation from dilute solutions in the presence of gelatin. The precipitated salt is peptized to a certain extent by a boiling concentrated solution of potassium nitrate.[24] If lead sulfate suspended in potassium nitrate solution is treated with potassium chromate, lead chromate is thrown out in the form of a greenish fluorescent sol.[25]

Lead chromate is a valued yellow pigment known as chrome yellow. The color varies from a light yellow to orange, depending on the conditions of precipitation and the subsequent treatment. The canary yellow product thrown down from a chromate solution with lead acetate or nitrate changes to an orange on washing. To maintain the desired yellow tone, the precipitation is carried out in the presence of sulfate so that lead chromate and lead sulfate come down simultaneously. The rôle of the lead salt has been attributed by Habich[26] to the formation of a double salt, $PbCrO_4 \cdot PbSO_4$ or $PbCrO_4 \cdot 2PbSO_4$, but the existence of such compounds has not been estab-

[23] Phot. arch., **37**, 321 (1896); "Chemische Reaktionen in Gallerten," Dusseldorf (1898); Z. anal. Chem, **50**, 82 (1911); Kolloid-Z, **9**, 296 (1911); **12**, 74, 269 (1913); **16**, 76 (1915); Z. physik. Chem., **88**, 1 (1914).

[24] Oeschsner de Coninck: Bull. acad. roy méd Belg., 665 (1909).

[25] Milbauer and Kohn: Chem.-Ztg., **46**, 1145 (1922).

[26] *See* Amsel: Z. angew. Chem., **9**, 613 (1896).

lished. Jablczynski [27] attributes the stabilizing action of lead sulfate to lead ions which cut down the hydrolysis of lead chromate thereby preventing the formation of "chrome red," basic lead chromate. This hypothesis appears untenable since lead sulfate exerts no stabilizing action unless it is precipitated simultaneously with the chromate. Moreover, lead sulfate is itself hydrolyzed appreciably,[28] and it is not obvious how it could prevent the hydrolysis of the chromate. Gobel [29] suggests that the lead sulfate prevents the coalescence of the fine yellow particles of lead chromate into larger particles which are darker in color.[30] This plausible suggestion is treated lightly by Milbauer and Kohn,[31] who conclude, from a microscopic examination of the crystals and the action of the solvents on them, that the stable yellow pigment is a solid solution of lead sulfate and lead chromate. Lead sulfate, being more soluble than lead chromate, has a greater tendency to come down in crystals from dilute solution. For this reason, it is argued that the technical production of chrome yellow is carried out in very dilute solutions and with continuous stirring in order to induce the simultaneous precipitation of the substances as mixed crystals.

The conclusions of Milbauer and Kohn have been confirmed and extended by Wagner [32] and by Quittner, Sapgir, and Rassudowa [33] using x-ray analytical methods. Under the usual conditions of precipitation lead chromate comes down in the form of extremely minute rhombic grains which appear bright yellow. The rhombic lead chromate is the least stable form and goes over into the more stable monoclinic modification which may possess an undesirable dark yellow color. Larger and stabler crystals of the rhombic chromate are formed as mixed crystals with lead sulfate under suitable conditions. The color is not alone a question of crystal structure since mixed crystals of $n\mathrm{PbCrO_4} \cdot m\mathrm{PbSO_4}$ having a bright yellow color may be either monoclinic or rhombic depending on the ratio of $m:n$. It is always monoclinic if the mixed crystals contain more than 50% of $\mathrm{PbCrO_4}$. The rhombic form may be stabilized by protecting colloids. For ex-

[27] Chem. Ind. (Ger.), **31**, 731 (1908).

[28] Dolezalek: Z. Elektrochem., **5**, 533 (1899); **6**, 557 (1900).

[29] Chem.-Ztg., **23**, 544 (1899).

[30] *Cf.* Free: J. Phys. Chem., **13**, 114 (1909); Bock: Farben-Ztg, **25**, 761 (1920); Wagner and Keidel: **31**, 1567 (1926).

[31] Z. physik. Chem., **91**, 410 (1916); Chem.-Ztg., **46**, 1145 (1922).

[32] Z. angew. Chem., **44**, 665 (1931); Wagner, Haug, and Zipfel: Z. anorg. Chem., **208**, 249 (1932).

[33] Z. anorg. Chem., **204**, 315 (1932); Sapgir, Rassudowa, and Kvitner: Lakokrasochnuyu Ind., Za, **1**, 56 (1932).

ample, in the precipitation of the mixed crystals, if lead nitrate is added to a mixture of dichromate and aluminum sulfate (instead of sulfuric acid) followed by careful post-precipitation of hydrous alumina with alkali, the rhombic crystals are surrounded by a film of hydrous oxide which inhibits the transformation to the rhombic form.[34]

The tetragonal form of lead chromate can be obtained in the form of orange-red mixed crystals with lead molybdate.

The products known as the "chrome reds" are bright red pigments formed by adding basic lead acetate to a solution of alkali chromate. Between these and the various "yellows," a number of different shades of chrome orange may be prepared.

The basic lead chromates formed by precipitation in the presence of alkali, or by the action of alkali on lead chromate, vary in color with the alkali concentration. With relatively low alkali concentrations there results first an orange-red color, then, with increasing alkali concentration, a pure red uniform product, and finally, a non-uniform product. Whatever the color, the product has the same composition $PbO \cdot PbCrO_4$ and gives the same x-radiogram,[35] the crystals belonging to the tetragonal system; variations in color are caused by differences in particle size and shape. If the basic chromate is allowed to stand in the mother liquor in contact with the air, a clear yellow double salt $K_2CO_3 \cdot PbCrO_4$ is formed. This may be converted into the orange-red basic salt by the action of alkali. The relationships among the three compounds may be represented as follows:

$$\underset{\text{Dark yellow}}{PbCrO_4} \xrightarrow{KOH} \underset{\text{Orange to red}}{PbO \cdot PbCrO_4} \underset{Ca(OH)_2}{\overset{KOH,\ K_2CrO_4,\ CO_2}{\longleftarrow}} \underset{\text{Clear yellow}}{K_2CO_3 \cdot PbCrO_4}$$

The lead chromate colors are ordinarily used as pigments in paints, but they may be precipitated directly on cellulose[36] or wool[36] fibers which adsorb them sufficiently strongly that the color is permanent. Yoshida and Matsumoto[37] claim that the crystals so produced belong to the tetragonal system.

[34] *Cf.* Bock: Farben-Ztg., **32**, 459 (1926).

[35] Wagner and Schirmer: Z. anorg. Chem., **222**, 245 (1935).

[36] Il'inskii and Kozlov: J. Russ. Phys.-Chem. Soc., **62**, 665 (1930).

[37] J. Soc. Chem. Ind., Japan, **38**, Suppl. Binding, 113 (1935); Matsumoto: **39**, 180 (1936).

COLLOIDAL ARSENATES

The Precipitated Salts

The addition of alkali arsenates such as KH_2AsO_4 to solutions of bivalent heavy metal salts gives precipitates that vary in form from gelatinous to jelly-like depending on the conditions. According to the von Weimarn theory (p. 11), mixing dilute solutions which interact at once to give a highly insoluble precipitate should give a gelatinous precipitate but not a jelly. The reason is evident when we consider the impossibility of getting the instantaneous mixing of the solutions, which is essential for uniform precipitation throughout the solution. One part is precipitated before another is mixed with the precipitant, and the homogeneity characteristic of a jelly is lost. Moreover, the mixing itself will tend to destroy the jelly structure. The results are therefore not unlike those obtained when a colloid, capable of forming a jelly by slow precipitation, is coagulated too rapidly by the addition of excess electrolyte (*cf.* Vol. II, p. 186). It would seem, however, that precipitation of a hydrous substance as a result of double decomposition might form a jelly instead of a gelatinous precipitate provided the thorough mixing of the solutions could be effected before precipitation began and provided the precipitation, once started, proceeded at a suitable rate. Such conditions do not obtain as a rule; but they are quite possible theoretically. Thus the precipitation may be the result of a stepwise reaction, one step of which proceeds at a suitably slow rate. It is further possible to have a reaction that proceeds very slowly at low temperatures but with marked velocity at higher temperatures. This would not only allow of mixing without precipitation but would also enable one to control the subsequent rate of reaction by a suitable regulation of the temperature.

Such a favorable combination of circumstances apparently obtains when a manganese salt of a strong acid and KH_2AsO_4 are mixed. The latter salt ionizes thus: $KH_2AsO_4 \rightleftarrows K^+ + H_2AsO_4^-$; but on account of the solubility of $Mn(H_2AsO_4)_2$ no Mn^{++} ions are removed from solution by interaction with $H_2AsO_4^-$. The latter ion, however, undergoes secondary ionization to a slight degree as follows: $H_2AsO_4^- \rightleftarrows H^+ + HAsO_4^{--}$; and insoluble $MnHAsO_4$ is formed in accord with the following equation: $Mn^{++} + HAsO_4^{--} \rightarrow MnHAsO_4$.[38]

Since the precipitation of $MnHAsO_4$ is accomplished by the formation of an equivalent amount of free hydrogen ion in solution, an

[38] Deisz: Kolloid-Z., **14**, 139 (1914).

equilibrium is set up which prevents the complete precipitation of the manganese. The amount of $MnHAsO_4$ formed, however, and the rate of formation by the above process are apparently influenced to a marked degree by the temperature, so that good jellies can be obtained by mixing dilute solutions of the necessary salts in the cold and allowing the mixture to stand at room temperature or warming to a suitable temperature. This has been demonstrated with the arsenates of manganese, cobalt, ferrous iron, cadmium, and zinc.[39] The results with manganese arsenate are recorded in Table X. Solutions of *N*

TABLE X

PRECIPITATION OF MANGANESE ARSENATE

Electrolytes mixed, cc		Final volume	Nature of precipitate
$MnCl_2$	KH_2AsO_4		
10	10	20	Firm jelly, almost clear
10	20	30	Firm jelly, almost clear
10	20	50	Firm jelly, perfectly transparent
10	20	100	Firm jelly, perfectly transparent
10	20	200	Soft jelly, perfectly transparent
10	20	300	No jelly
	NaH_2AsO_4		
10	10	20	Cloudy jelly, not uniform
10	10	50	Cloudy gelatinous precipitate

$MnCl_2$ and KH_2AsO_4 were prepared from freshly boiled water. This precaution was necessary to prevent the formation of air bubbles in the jelly. The solutions were cooled to 0° and suitable amounts of each were placed in 60-cc test tubes in the ratio shown in the table. The solutions were diluted with cold water to the final volume shown in column 3 or an aliquot part thereof. After rapid mixing, the solution was set aside for 15 to 20 minutes and, if jelling had not begun, the tube was warmed by dipping carefully into boiling water until precipitation started and was then allowed to stand quietly. The jellies obtained in this way are quite stable, showing little tendency to cloud up and crystallize on standing in the cold; but on heating, crystals of $MnHAsO_4$ are formed. Good jellies are not obtained with

[39] Weiser and Bloxsom: J. Phys. Chem., **28**, 32 (1924).

Na_2HAsO_4 since the precipitation is too rapid to allow time for mixing and the formation of the jelly structure.

Arsenate Sols

The addition of excess ferric chloride to a normal solution of disodium arsenate gives a sol which is said to be $Fe_2(HAsO_4)_3$ but which may be, at least in part, an adsorption complex of hydrous ferric oxide and arsenic oxide. This sol is precipitated as a jelly either by dialysis [40] until the concentration of the stabilizing hydrogen ion is reduced below a critical value or by the addition of a precipitating electrolyte.[41] The so-called aluminum arsenate sol prepared in the same way as the iron sol exhibits similar properties.

The most important colloidal arsenates are the calcium and lead salts which are dusted or sprayed on plants or trees for the purpose of destroying insects. If the finely divided precipitated salts are suspended in water they assume a negative charge. Since the surfaces of leaves possess a like charge, the insecticide does not adhere to them readily and is soon washed off by rain or dew. The particles of salt adhere much more tenaciously if they are prepared in such a way that they adsorb a positive ion which gives them a positive charge when wet. Thus, a positively charged basic calcium arsenate made under commercial manufacturing conditions, not specified, and tested in the field was found to possess an adherence from 200 to 260% greater than the ordinary precipitated salt.[42]

The lead arsenate precipitated from lead nitrate solution with disodium arsenate is the acid salt which does not become positively charged under ordinary conditions. On the other hand, the basic salt thrown down from lead acetate solutions readily assumes a positive charge.[43] The acid arsenate is assimilated to a greater degree than the basic arsenate; hence the former possesses higher insecticidal efficiency.[44] The acid salt may be made adherent by coating the fine particles with a film of lead oleate.[45] This is accomplished by suspending the salt in

[40] Grimaux: Compt. rend., **98**, 1540 (1884); Holmes and Rindfusz: J. Am. Chem. Soc., **38**, 1970 (1916); Holmes and Arnold: **40**, 1014 (1918); Holmes and Fall: **41**, 763 (1919).

[41] Weiser and Bloxsom: J. Phys. Chem., **28**, 26 (1924).

[42] Moore: Ind. Eng. Chem., **17**, 465 (1925); J. Econ. Entomol., **18**, 282 (1925).

[43] Moore: Ind. Eng. Chem, **17**, 466 (1925).

[44] Lovett: Oregon Agr. Expt. Sta. Bull., **169**, 1 (1920); Chem. Abstracts, **15**, 3718 (1921).

[45] Van Leeuwen: J. Econ. Entomol., **18**, 744 (1925).

water containing a known amount of sodium oleate and adding an equivalent amount of lead acetate with vigorous stirring. The dried product is not wetted by water, but the suspension spreads evenly on foliage and adheres firmly to the surface. The charge on the acid arsenate particles may be rendered positive and adherent to negative surfaces by the addition of a suitable amount of aluminum ion.[46]

Woodman[47] demonstrated that leaves can be wetted by a spray liquid provided the surface tension is reduced below a critical value said to be in the neighborhood of 32 dynes/cm.[48] This can be accomplished cheaply by the addition of a small amount of soap. The maximum amount of spray liquid is retained at a critical surface tension; at higher tensions the wetting of the leaves is imperfect, and at lower values the wetting power is not increased but the spreading power is greatly augmented. After the surface tension has been reduced to the point where the foliage is wetted perfectly, an increase in the viscosity of the spray liquid causes an increase in the amount of liquid retained as a film by the leaves; hence the use of gelatin in concentrations of about 0.3% is advantageous. Moreover, gelatin[49, 47] in concentrations between 0.2 and 0.5% is a better stabilizer for lead arsenate sols than sodium caseinate, dextrin, starch, or soap.

[46] Hensill and Hoskins: J. Econ. Entomol., **28**, 942 (1935); Hoskins and Wampler: **29**, 135 (1936).

[47] J. Pomology Hort. Sci., **4**, 78, 95, 184 (1925).

[48] *Cf., however,* Robinson: J. Agr. Research, **31**, 71 (1925).

[49] Brinley: J. Agr. Research, **26**, 373 (1923).

Part II

THE COLLOIDAL HALIDES

CHAPTER VI

COLLOIDAL SILVER IODIDE

Precipitated Silver Iodide

The silver halides are sufficiently insoluble that they are ordinarily precipitated in the form of curds of minute crystals on mixing cold solutions of alkali halide and silver nitrate. Silver iodide, which is less soluble (9.7×10^{-9} mol/l) than either the bromide (6.6×10^{-7} mol/l) or the chloride (1.25×10^{-5} mol/l), comes down in the most finely divided form under the same conditions of temperature and concentration of reacting solutions. All three halides are sufficiently soluble that the colloidal precipitates which are first formed age rather rapidly on standing to give agglomerates of crystals which are larger and more perfect, and possess a lower adsorption capacity than the freshly formed curds. The rate of aging of the salts is in the order: $AgI < AgBr < AgCl$, which is the reverse of the order of the stability of the gels and sols of the halides.

The precipitation of silver halides in the absence of an excess of either positive or negative ions is attributed by Lottermoser to coagulation of the particles into larger secondary aggregates which settle out. Jablczynski[1] objects to this mechanism of the precipitation on the ground that it does not explain the velocity of increase of turbidity in the presence of gelatin or other protecting colloids which inhibit precipitation even in low concentrations. The view held by Jablczynski is that the formation of a precipitate and the process of grain growth, both in the presence and in the absence of gelatin, are entirely a process of recrystallization by solution of the smaller grains and growth of larger ones at their expense (Ostwald ripening) until the larger grains are thrown down. This contention of Jablczynski is contradicted by Sheppard and Lambert's[2] observations of reversible flocculation and deflocculation of a part of the silver halides precipitated in the absence

[1] Jablczynski, Fordonski, Frankowski, Lisiecki, and Klein: Bull. soc. chim, (4) **33**, 1392 (1923).

[2] Colloid Symposium Monograph, **4**, 281 (1926).

of gelatin, and by microscopic examination which reveals the presence of secondary aggregates consisting of loosely adhering primary particles. In the absence of protecting colloids, it thus appears that aggregation is the important factor in causing precipitation, although some recrystallization does take place; whereas, in the presence of protecting colloids, the coagulation is largely inhibited, at least until high concentrations of the reactants are used. The grain growth observed in the ripening of photographic emulsions is caused primarily by a process of recrystallization from solution in which crystal aggregation plays but a minor rôle.[3]

The crystals of silver iodide thrown down in the presence of excess Ag^+ ion are cubic whereas those precipitated in the presence of excess I^- ion are hexagonal.[4]

Adsorption by Silver Iodide

Adsorption of Silver Ions and Iodide Ions. Lottermoser[5] first called attention to the fact that sols are formed on mixing dilute solutions containing silver ions and halide ions provided one or the other is present in excess; with silver ions in excess the particles are positively charged, and with iodide ions in excess the particles are negatively charged. The charge results from the preferential adsorption of the potential-determining ions:[6] silver with the positive sol and iodide with the negative sol. Since the range and degree of stability of negative sols are greater than those of positive sols (p. 114) it would appear that iodide ion should be more strongly adsorbed than silver ion. This is borne out by some observations of Lottermoser and Rothe[7] on the adsorption of potassium iodide and silver nitrate, respectively, by precipitated and thoroughly washed silver iodide. The adsorption of iodide reaches a maximum which is considerably greater than that of silver nitrate at the same concentration. The maximum in the adsorption isotherm of potassium iodide is caused by growth of the silver iodide crystals in the presence of the larger amounts of potassium salt (*cf.* with the behavior of cadmium sulfide in the presence of hydrochloric acid, p. 256). Even in very low concentrations iodide ion appears to be adsorbed more strongly than silver ion since

[3] Sheppard: Colloid Symposium Monograph, **1**, 346 (1923).

[4] Bloch and Moller: Z. physik. Chem., **A152**, 245 (1931); Kolkmeijer and Hengel: Z. Krist., **88**, 317 (1934).

[5] J. prakt. Chem., (2) **72**, 39 (1905).

[6] Lange and Berger: Z. Elektrochem., **36**, 171 (1930).

[7] Z. physik. Chem., **62**, 359 (1908).

Lange and Crane [8] showed that aged and very thoroughly washed silver iodide is negatively charged in contact with its saturated solution. On the other hand, Lange and Berger [9] concluded from potentiometric titration experiments that silver ions are more strongly adsorbed than iodide ions at equal equilibrium concentrations. But as Kolthoff and Lingane [10] point out, this conclusion was based on the erroneous assumption that neither silver nor iodide ions are adsorbed at the potentiometric end point where $C_{Ag^+} = C_{I^-}$ in solution. It was demonstrated by Kolthoff and Lingane that the isoelectric point of freshly precipitated silver iodide at room temperature is at a silver ion concentration of approximately 10^{-6} molar ($p\mathrm{Ag} = 6$) and that, at the equivalence potential, $p\mathrm{Ag} = p\mathrm{I} = 7.83$, the freshly formed precipitate retains an excess of adsorbed iodide corresponding to 0.09% of the total amount of iodide in the precipitate. This conclusion was based on precision potentiometric titrations of silver with iodide from which the adsorption of silver and iodide ions was calculated by comparing the experimentally determined titration curve with the theoretical curve based on the assumption that the precipitate has no adsorptive properties. The results are shown graphically in Fig. 16.

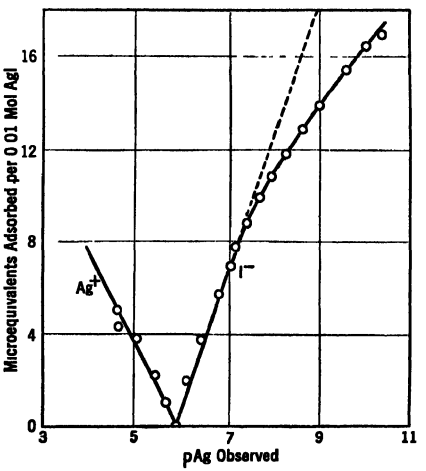


FIG. 16.—Adsorption of silver and iodide ions by freshly precipitated silver iodide.

In investigating the precision of the potentiometric silver iodide titration, Lange and Berger showed that the adsorption of both silver and iodide ions is represented by the expression $dx = a\,d\log c$ instead of by the Freundlich equation, $d\log x = a\,d\log c$, where x is the amount adsorbed, a is a constant, and c is the equilibrium concentra-

[8] Z. physik. Chem., **A141**, 225 (1929); *cf*, *also*, Labes: Z. physik. Chem., **116**, 1 (1925); Kruyt and van der Willigen: **A139**, 53 (1928); Mukherjee and Kundu: J. Indian Chem Soc., **3**, 335 (1926).

[9] Z. Elektrochem., **36**, 171, 980 (1930).

[10] J. Am. Chem. Soc., **58**, 1524, 1528 (1936).

tion of the ion being adsorbed. Similarly, the adsorption data given in Fig. 16 can be represented by the equation $dx = a\,d\log c$ in the pAg range between 4 and 7.2, but at higher values the adsorption is less than corresponds with this equation, probably because of the rapidity with which fresh precipitates of silver iodide age in contact with potassium iodide. As we shall see, Verwey and Kruyt [11] found that the equation applies to the adsorption of iodide by an aged silver iodide sol over a much wider range than Kolthoff and Lingane found with a fresh precipitate. Verwey and Kruyt could not measure directly the isoelectric point without flocculation of the sols, but with the aid of the above equation they extrapolated to the point of zero adsorption (isoelectric point) and found it to be at $p\text{Ag} = 6$, in good agreement with the value found directly by Kolthoff and Lingane. On the other hand Kruyt [12] showed by endosmotic experiments that fused silver iodide cannot be charged positively even with 0.001 N $AgNO_3$. It appears, therefore, that the zero point of the electrokinetic charge depends on the nature of the silver iodide. In aged dialyzed sols the charge is reversed at $p\text{Ag} = 6$.

From exhaustive studies of the precision of the iodide-silver potentiometric titration, Lange and Berger [9] concluded that the titration should give results accurate to $\pm 0.01\%$ if made under the most favorable conditions. The titration was found to be altogether impractical when carried out at room temperature because of strong adsorption of silver and iodide ions by the voluminous precipitate and the consequent slowness with which a steady e.m.f. was attained. These objectionable effects of adsorption were practically eliminated by titrating at 90° where an aged precipitate of low adsorption capacity results.

Lange and Berger's results were confirmed and the accuracy of the method established by Kolthoff and Lingane working with highly purified reagents. In the slow titration of silver with iodide, the error at room temperature amounts to 0.1%; at 70°, to 0.048%; and at 90°, to 0.017%. By digesting the precipitate at 90° near the equivalence point, and finishing the titration at room temperature, the error was 0.028%. In every precipitate an excess of iodide was adsorbed at the equivalence point.

Hönigschmid and Striebel [13] determined the atomic weight of iodine by means of silver iodide. One sample precipitated in nitric

[11] Z physik. Chem., **A167**, 149 (1933); Verwey: Kolloid-Z., **72**, 187 (1935).
[12] Physik. Z. Sowjetunion, **4**, 295 (1933).
[13] Z. anorg. Chem., **208**, 53 (1932).

acid solution with excess silver ion, washed, dried, and fused, did not contain enough excess silver to be detected.

Adsorption of Inorganic Ions and Paneth-Fajans' Rule. In an earlier chapter (p. 34) attention was called to Paneth's [14] observation that radium is strongly adsorbed by barium sulfate and chromate whereas it is not adsorbed at all by chromic oxide or silver chloride. Since radium sulfate and chromate are insoluble and radium oxide and chloride are soluble, Paneth formulated the adsorption rule for radio elements: ions will be relatively strongly adsorbed if the compound with the oppositely charged ions of the crystal lattice is slightly soluble. This rule was confirmed and extended by Fajans and his coworkers [15] to include elements other than radio elements. The original Paneth-Fajans rule may be stated as follows: ions will be strongly adsorbed on an ion lattice which form a difficultly soluble or weakly dissociated compound with the oppositely charged ion of the lattice. An important example of this rule, the strong adsorption of common ions by an ion lattice, was considered in the preceding section. In further accord with the rule, Fajans and Beckerath found that both thorium B and lead ions are quite strongly adsorbed by silver halide made negative by preferential adsorption of halide ion, and it is known that the halides of thorium B and lead are not easily soluble. Moreover, the adsorption of thorium B is greater than that of lead, and the halides of the former are less soluble than those of the latter. Fajans and Beckerath showed further that thorium B and lead ions are not adsorbed by a silver halide made positive by preferential adsorption of silver ion. This is because the adsorption of thorium B at the concentration used is not sufficiently great to displace the more strongly adsorbed silver ions.

Beekley and Taylor [16] investigated the relation between the solubility of various silver salts and their adsorbability by silver iodide. The effect of valence was eliminated by choosing salts with univalent anions only. The results of their observations are represented in Fig. 17. The number in parentheses following the formula of the salt

[14] Paneth: Physik. Z., **15**, 924 (1914); Horovitz and Paneth: Z. physik. Chem., **89**, 513 (1915).

[15] Fajans and Beer: Ber., **46**, 3486 (1913); Fajans and Richter: **48**, 700 (1915); Fajans and Beckerath: Z. physik. Chem., **97**, 478 (1921); Fajans and Frankenburger: **105**, 255 (1923); Fajans and Sterner: **125**, 309 (1927); Fajans and Erdey-Grúz: **A158**, 97 (1931).

[16] J. Phys. Chem., **29**, 942 (1925); *cf.* Mukherjee, Basu, and Mukherjee: J. Indian Chem. Soc., **4**, 459 (1927); Chakravarti and Dhar: Kolloid-Z., **45**, 12 (1928).

is the relative solubility, silver bromate, the most insoluble salt, being taken as unity. It will be seen that a quantitative relationship between solubility and adsorbability is not approached. The most that can be said is that the less soluble salts tend to be more strongly adsorbed and the more soluble salts less strongly adsorbed. Among the more soluble ones, silver nitrate, though nineteen times as soluble, is adsorbed more strongly than silver chlorate; and among the less soluble ones, silver acetate, though eight times as soluble, is adsorbed much more strongly than silver bromate. Moreover, the jump in adsorption between the relatively insoluble and relatively soluble salts is not

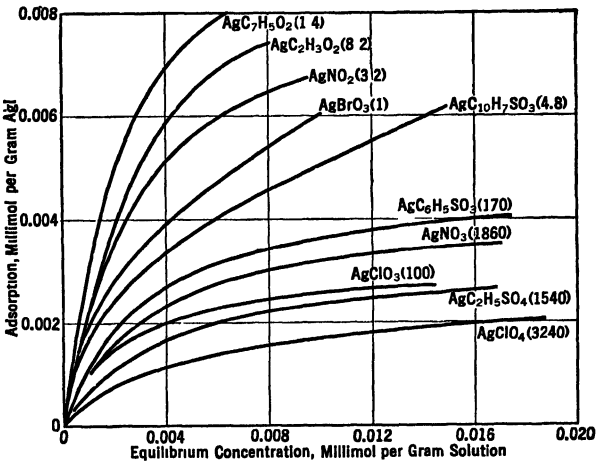


FIG. 17—Adsorption of silver salts by silver iodide. (Number in parentheses is the relative solubility of the silver salts)

marked; *e.g.*, the difference in adsorption between bromate and acetate is no greater than the difference in adsorption between bromate and nitrate, although the ratio of solubilities of the first pair is 8.2 and that of the second pair is 100.

From these observations and others already mentioned (p. 29) it is obvious that solubility is not the only factor which determines the degree of adsorption of ions on ion lattices and may not be the most important one in certain cases. Fajans considers adsorption of ions by a crystal to take place through the agency of the residual valences of the ions on the surface of the lattice. Thus, when iodide ion is adsorbed on silver iodide, it becomes attached to the silver ion and

so becomes an integral part of the silver iodide lattice. In so doing the adsorbed ion loses its hydration shell,[17] the dehydration being accompanied by a marked energy change. From this point of view it would follow that, the greater the affinity of an ion for water, in other words the more highly hydrated it is, the less strongly it will be adsorbed (p. 352). A third factor which must be taken into account is the relative size of the adsorbed and the lattice ions, irrespective of whether the ions are adsorbed directly on the surface or enter into kinetic interchange with an ion on the surface (p. 54). A fourth factor is the deformation which an ion undergoes in a field of force. In general, the more readily deformable an ion the better it will be adsorbed to the oppositely charged ion of the lattice.[18]

In opposition to the Paneth-Fajans rule in its original form Hahn and Imre[19] observed a number of cases in which a radio element is not adsorbed even when it forms a difficultly soluble compound with the oppositely charged ion of the lattice. For example, the failure of thorium B to be adsorbed appreciably by positively charged silver halide is cited as being in opposition to the rule since thorium B forms sparingly soluble halides. Also oxalate ion is not appreciably adsorbed by silver bromide and silver iodide, and chloride is not adsorbed very strongly by silver iodide. Hahn attempted to make the adsorption rule more general by the following formulation: an ion in dilute solution is adsorbed on a precipitate if the surface of the precipitate has a charge opposite to that of the ion being adsorbed and if the resulting compound is difficultly soluble in the solvent. It would follow from this that a neutral surface would adsorb only ions common to the lattice or isomorphous with it.[20] In opposition to this Fajans[21] showed that certain organic dye ions, thorium B cation, as well as certain non-radioactive inorganic ions, may be concentrated on an adsorbent which does not exhibit a charge opposite to that on the ion. For example, thorium B is adsorbed by silver iodide, chromate, oxalate, and phosphate even when positively charged by adsorption of a slight excess of silver ion. Also, certain dye anions are adsorbed on negatively charged silver halide and dye cations on positively

[17] Fajans: Naturwissenschaften, **9**, 733 (1921); Z. Krist., **66**, 321 (1928); *cf.* Lange and Crane: Z. physik. Chem., **A141**, 225 (1929).

[18] Fajans: Z. Krist., **66**, 321 (1928).

[19] Hahn: Ber., **59B**, 2014 (1926); Naturwissenschaften, **14**, 1196 (1926); Hahn and Imre: Z. physik. Chem., **A144**, 161 (1929).

[20] Hahn: Z. angew. Chem, **43**, 871 (1930).

[21] Fajans and Erdey-Grúz: Z. physik. Chem., **A158**, 97 (1931).

charged silver halide. It should be recalled that a neutral surface is seldom encountered except in the presence of some electrolyte; thus we have seen that silver iodide forms an equivalent compound only in the presence of a small excess of silver nitrate. In this connection Fajans and Erdey-Grúz have made an extended study of the effect of the presence of various electrolytes on the adsorption of thorium B by silver bromide, iodide, sulfide, iodate, chromate, oxalate, and phosphate. The results show that strongly adsorbed cations cut down, and strongly adsorbed anions increase, the adsorption of thorium B. The adsorption on silver iodide, for example, is increased by the presence of anions in the order: $I > CNS > Br > Cl$, which is the same as the order of adsorption of these ions on the silver halide. In the presence of the strongly adsorbed hydrogen ion, the adsorption is less than in neutral solution.

In the light of these and similar observations Fajans formulates what may be termed the Paneth-Fajans-Hahn rules: (*a*) An ion is strongly adsorbed on an equivalent compound of the salt type only when it forms a difficultly soluble or weakly ionized compound with the oppositely charged ion of the lattice. (*b*) The adsorption of a cation is raised by adsorbed anions, that is, by charging the surface negatively, and is lowered by adsorbed cations, that is, by charging the surface positively. (*c*) The adsorption of anions is raised by adsorbed cations and is lowered by adsorbed anions. The effects in both (*b*) and (*c*) increase with increasing adsorption of the added ions. These rules will probably hold in most cases of adsorption on ion lattices provided one also takes into account the hydration, size, and deformability of the adsorbed ions. There is nothing new about rules (*b*) and (*c*). These facts were first recognized by Lachs and Michaelis [22] and by Estrup [23] and have been worked out in detail for the process of dyeing on fibers by Pelet-Jolivet,[24] by Bancroft,[25] and by Briggs and Bull;[26] and for the mordanting process on hydrous oxide mordants by Weiser and Porter [27] (Vol. II, Chapter XVI).

The order of adsorption of cations by silver iodide was found by Mukherjee and Kundu [28] to be: $Ag > Al > Ba > Ca > K$. With the

[22] Z. Elektrochem., **17**, 1 (1911).
[23] Kolloid-Z., **11**, 8 (1912).
[24] "Die Theorie des Farbeprozesses," 94, 98, 119, 148 (1910).
[25] J. Phys. Chem., **18**, 1, 118, 385 (1914).
[26] J. Phys. Chem., **26**, 845 (1922)
[27] J. Phys. Chem., **31**, 1383, 1704, 1824 (1927); Weiser: **33**, 1713 (1929).
[28] J. Indian Chem. Soc., **3**, 335 (1926).

exception of the common silver ion, the ion with the highest valence is the most strongly adsorbed.

In this connection may be mentioned the observation of Frumkin and Obrutschewa [29] that silver iodide exhibits a maximum adsorption for caprylic alcohol at a silver ion concentration of a definite strength corresponding to 0.16 volt as measured with a silver electrode against a normal calomel electrode.

Carey Lea [30] claimed that freshly precipitated silver iodide adsorbs iodine from an alcohol-water solution of the element, but Germann and Traxler [31] found that this is not so. A thoroughly purified sample of the salt does not decolorize a dilute iodine solution; this results only when the sample is not washed so as to remove adsorbed silver nitrate which will react with iodine.

Adsorption of Dye Ions. The silver halides adsorb dyes both from true and from colloidal solutions [32] and also adsorb organic colloids such as casein, tannin, gums, and gelatin.[33] The adsorption of dyes is of special interest and importance because of the use of dyes in the sensitizing of the photographic plate (p. 150) and the application to adsorption indicators in analytical titrations. Since the principle of titration by means of adsorption was worked out by Fajans in connection with silver bromide, the discussion of adsorption indicators will be taken up in the next chapter (p. 132).

The adsorption of dye ions on the silver halides is, in general, in accord with the Paneth-Fajans-Hahn rules.[21] Thus the silver salt of the acid dye eosin is fifty times as soluble as the silver salt of the acid dye erythrosin, and erythrosin is adsorbed by silver bromide much more strongly than eosin. Moreover, the presence of electrolytes with a common cation and different anions cuts down the adsorption of acid dyes in proportion to their adsorbability on the salt in question. This is illustrated by the effect of potassium salts on the adsorption of erythrosin by silver iodide as shown graphically in Fig. 18. From the displacing power of the anions one would deduce the order of adsorption to be: $I > CNS > Br > Cl$. This same order would be deduced from the solubilities of the respective silver salts except that thiocyanate is adsorbed more strongly than bromide although silver thiocyanate is more soluble than silver bromide (p. 114).

[29] Biochem. Z., **182**, 220 (1927).
[30] Am. J. Sci., (3) **33**, 492 (1887).
[31] J. Am. Chem. Soc., **44**, 460 (1922).
[32] *Cf* Luppo-Cramer: Kolloid-Z., **28**, 90 (1921).
[33] Reinders: Z. physik. Chem., **77**, 677 (1911).

The presence of silver nitrate increases greatly the adsorption of acid dyes by the silver halides (p. 133).

Mechanism of the Adsorption. The adsorption phenomena above mentioned were observed with precipitated and thoroughly washed, hence with aged, silver iodide. The adsorption of a common ion by such a precipitate is a true adsorption as distinct from an exchange adsorption. Just as in the adsorption of thorium B on lead sulfate, Verwey and Kruyt [34] showed that iodide ion is not adsorbed over the entire surface but only at certain active spots on the surface. Indeed Kruyt [35] showed by endosmotic experiments that fused silver iodide which has relatively few corners and edges cannot be charged

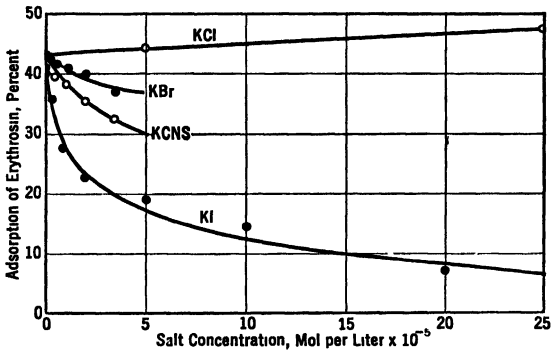


FIG. 18.—Effect of potassium salts on the adsorption of erythrosin by silver iodide.

positively even with 0.001 *N* $AgNO_3$. Just as in the adsorption of wool violet on lead sulfate, one may have exchange adsorption of the foreign anion, say, followed by precipitation with a corresponding amount of the lattice cation (p. 56).

In the adsorption of foreign ions, it is probable that an exchange takes place between the foreign ion and the lattice ion or between the foreign ion and the counter ion associated with another adsorbed ion. In the adsorption of erythrosin anion on negative silver iodide, it is probable that the dye anion enters into ionic exchange with iodide. In the adsorption of erythrosin on silver iodide which is positively charged by preferential adsorption of silver from silver nitrate, the anion probably enters into exchange adsorption with the counter nitrate

[34] Z. physik. Chem., **A167**, 149 (1933).
[35] Physik. Z. Sowjetunion, **4**, 295 (1933).

ion; and in the adsorption of lead ion by silver iodide which is negatively charged by preferential adsorption of iodide ion from hydriodic acid, the lead ion enters into exchange adsorption with the counter hydrogen ion.[36] As we shall see in the next chapter, the action of adsorption indicators may be interpreted as exchange adsorption rather than as direct adsorption.

Imre[37] studied the aging of silver halide precipitates, especially of silver iodide, following the time course of the adsorption by means

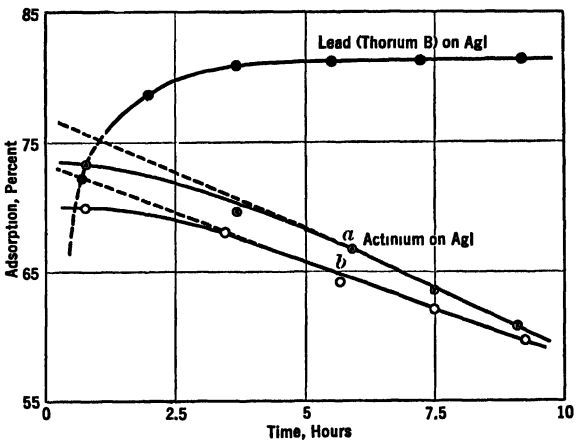


FIG 19.—The time course of the adsorption of thorium B and actinium by freshly precipitated silver iodide.

of the radioactive indicator method used in a study of the aging of barium sulfate (p. 35). As radioactive indicators were used thorium B, which forms insoluble lead iodide, and actinium and radium, each of which forms an easily soluble iodide. Some typical observations are shown graphically in Fig. 19. With thorium B which forms an insoluble compound, the adsorption value increases very slowly in spite of the marked decrease in the specific surface with time; on the other hand, the adsorption value of actinium which forms a soluble iodide falls off appreciably from the beginning. To account for this difference in behavior, it is assumed that the structure of the aging particles opens up because of the crystallization tendency thus enabling an ex-

[36] Verwey and Kruyt: Z. physik. Chem., **A167**, 312 (1933).

[37] Z. angew. Chem., **43**, 875 (1930); Z. physik. Chem., **A153**, 127 (1931); *cf.* Kolthoff and Yutzy: J. Am. Chem. Soc., **59**, 1215 (1937).

change reaction to take place in the immediate vicinity of the lattice. This accounts for the increasing adsorption of thorium B with time since the cations which form easily soluble halides remain in the outer diffuse portion of the double layer. It would follow that the adsorption phenomenon on freshly formed, highly dispersed precipitates involves two processes: the first process of momentary adsorption consists in an exchange adsorption of ions that depends on the surface charge and the valence of the adsorbed ion; the second process consists of a building up of molecules and resolution of the same at the surface layer. In the latter process the velocity of the decrease of surface and the insolubility of the adsorption compound are the important factors.

Silver Iodide Sols

The Electrical Double Layer

Nature. The older concept of the double layer at the interface solid-solution assumed it to consist of two "mono-ionic" layers of opposite charge touching each other at the boundary plane.[38] The modern theory due to Gouy [39] assumes that the total potential drop caused by the double layer occurs in the outer liquid portion which consists of a diffuse layer of ions. Stern [40, 41] assumes that part of the ions remain attached to the surface and part are free to move. He thus takes into account the size and physical properties of the ions constituting the outer layer. The attached ions are held by electrostatic and physical forces which differ for each ion, that is, each ion possesses a specific adsorption potential. Extending Gouy's views, Smoluchowski [42] assumes a continuous drop in potential in both the solid and liquid phases. This was confirmed by calculations of Verwey [43] from data obtained with a purified, well-aged silver iodide sol. The results are represented diagrammatically in Fig. 20. Part of the potential drop from E_0 to E is in the liquid phase and part in the solid. The part of the potential in the liquid phase ψ consists of (1) the potential in the mobile portion of the outer layer, the ζ-potential, and (2) the

[38] Helmholtz: Pogg. Ann., **89**, 211 (1853); *cf.* Perrin: J. chim. phys., **2**, 601 (1904); **3**, 50 (1905).

[39] J. phys., (4) **9**, 457 (1910); Ann. phys., (9) **7**, 129 (1917); Chapman: Phil. Mag., (6) **25**, 475 (1913); Herzfeld: Physik. Z., **21**, 28, 61 (1920); Debye and Huckel: **24**, 185, 305 (1923).

[40] Z. Elektrochem., **30**, 508 (1924).

[41] *Cf, also,* Janssen: Physik. Z. Sowjetunion., **4**, 322 (1933).

[42] Graetz's "Handbuch der Elektrizität und des Magnetismus," **2**, 366 (1914).

[43] Rec. trav. chim., **53**, 933 (1934).

potential in the attached portion of the outer layer, $\psi - \zeta$. Verwey points out that the conditions for an aged silver iodide sol, represented in Fig. 19, are relatively simple. The potential curve may be more complicated, sometimes containing a maximum or a minimum. But even if one disregards these complications, it is usually very difficult to find a relation between the different parts of the total potential drop. Such information would be particularly helpful since the stability of lyophobic sols depends on the ζ-potential which in turn is connected with the potential in the other parts of the double layer.

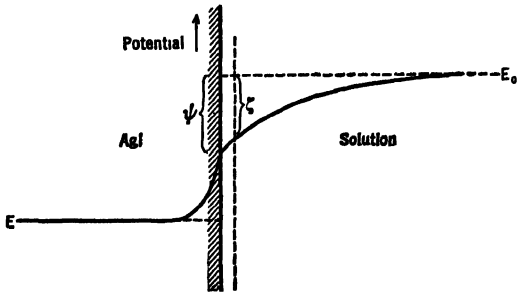


FIG 20.—Schematic curve for the potential perpendicular to the surface silver iodide-solution, for a dialyzed silver iodide sol.

Formation. If one takes the relatively simple case of silver iodide suspended in dilute hydriodic acid, a double layer is set up as a result of the adsorption of iodide ion on the surface of the silver iodide. The adsorbed iodide constitutes the inner portion of the double layer, and the counter hydrogen ion the outer diffuse portion. For electrostatic reasons, the negative charge like the equal positive charge in the solution is localized in the immediate neighborhood of the boundary layer and the potential drop caused by the double layer is in the same region. The potential difference between silver iodide and the solution is thus determined by a distribution of the common iodide ions over both phases. Ions which both phases have in common, and which are subjected to a distribution equilibrium to give the double layer, are called potential determining ions, after Lange.[6] For a silver iodide electrode at equilibrium, the potential E is given, in accord with the classical work of Nernst and of van Laar,[44] by the equation:

$$E = E_0 - \frac{RT}{F} \ln c_{I^-}$$

[44] Van Laar: "Lehrbuch der theoretischen Elektrochemie" (1907).

Furthermore, if E_0 is the total potential drop silver iodide-solution and c_0 the equilibrium concentration of iodide ions at the point of zero charge, then

$$E - E_0 = \frac{RT}{F} \ln \frac{c_0}{c_{I^-}} = 0.058 \log \frac{c_0}{c_{I^-}}$$

For a constant capacity of the double layer the amount of iodide adsorbed x by 1 g of AgI is proportional to $E - E_0$, hence

$$x = a_1 + a_2 \log c_{I^-}$$

in which a_1 and a_2 are fixed by the location of the zero point of charge and by the adsorption capacity which is given by the equation:

$$\frac{dx}{d\log c_{I^-}} = a_2 \quad \text{or} \quad dx = a\, d\log c_{I^-}$$

As already pointed out, the adsorption of potential-determining ions such as iodide and silver on silver iodide is represented by the equation $dx = a\, d\log c$ instead of by the Freundlich equation $d\log c = a\, d\log c$ where x is the amount adsorbed per gram of adsorbent and c is the equilibrium concentration. Verwey [45] refers to this taking up of potential-determining electrolytes, with the formation of a double layer, as a process of assimilation rather than as one of adsorption. Gibbs [46] points out that an electrolyte lowers the surface tension when it is positively adsorbed and raises the surface tension when it is negatively adsorbed. Since the taking up of potential-determining electrolytes does not satisfy Gibbs' criterion, Verwey contends that it is not an adsorption phenomenon. The difference is that one ion of the potential-determining electrolyte goes from the solution onto the solid phase causing a surface charge which theoretically could be effected from within this phase by the application of an external electric current. The surface tension is therefore not connected directly with the accumulation of electrolyte in the boundary layer but only indirectly as a result of the charge of the double layer thus formed; hence the process is not an adsorption. Similarly, it is argued that the exchange of lattice and counter ions should not be called adsorption. True adsorption of an electrolyte, according to Verwey, consists in the accumulation as a whole of an electrolyte in that part of the solution which is nearest the surface; it is therefore not accompanied by a change of the total boundary potential drop.

[45] Chem. Rev., **16**, 363 (1935); Wis-Natuurkund. Tijdschrt., **7**, 89 (1934).
[46] "Thermodynamics," Longmans-Green (1906).

The author prefers not to be as logical as Verwey and will continue to refer to the concentration of potential-determining ions at surfaces and to the exchange of lattice and counter ions as adsorption phenomena. True adsorption of indifferent electrolytes at ion lattices in the sense of Verwey appears to be encountered rarely if at all. It will be recalled that de Brouckère claimed to get equivalent adsorption of cations and anions at a barium sulfate surface, but this is denied by Kolthoff (p. 32). The taking up of ions from indifferent electrolytes appears to be represented by the Freundlich equation $d\log x = a\, d\log c$ [47] rather than by the equation $dx = a\, d\log c$ which holds for the adsorption of potential-determining ions.

The essential difference between the building up of a double layer by adsorption of potential-determining ions and the formation of a double layer by adsorption of electrolytes is that, in the first, the potential-determining ions are assimilated into the surface in accord with the equation $dx = a\, d\log c$, whereas, in the latter, the ions are merely oriented in the solution nearest the surface in accord with the equation $d\log c = a\, d\log c$. It is assumed by Verwey that the building up of the primary double layer by assimilation of potential-determining electrolyte is required for the primary stability of sols. It follows from this that the adsorption of potential-determining ions only, will peptize a substance; the adsorption of indifferent ions will not cause the primary stability but will influence the stability of a sol once formed.

Preparation

Peptization by Common Ions. From the preceding section it would follow that electrolytes containing the common silver and iodide ions would be the best peptizing agents for silver iodide sols. This classical method of Lottermoser [48] consists essentially in adding a suitable excess of one of the reacting salts, silver nitrate and alkali halide, to a suspension of the freshly precipitated silver halide. For example,[49] if 0.1 *N* $AgNO_3$ is allowed to drop from a buret into 500 cc of 0.002 *N* KI stirred by a motor stirrer, the first drop gives a green-yellow, perfectly transparent sol which becomes gradually more and more opales-

[47] Janssen: Physik. Z. Sowjetunion, **4**, 322 (1933); Kruyt and van der Willigen· Kolloid-Z., **45**, 307 (1928).

[48] J. prakt. Chem., (2) **56**, 241 (1897); **68**, 341 (1903); **72**, 39 (1905); **73**, 374 (1906); Z. physik. Chem., **60**, 451 (1907); **70**, 239 (1910).

[49] Lottermoser, Seifert, and Forstmann: Kolloid-Z. (Zsigmondy Festschrift), **36**, 230 (1925).

cent with further additions of iodide until, at approximately the equivalence point between iodide and silver, the opalescence increases rapidly, the solution becomes cloudy, and an additional drop causes flocculation of the silver iodide. If the process is reversed and 0.1 *N* KI is allowed to drop slowly into 0.004 *N* $AgNO_3$, the phenomena are similar except that the clouding takes place somewhat more rapidly. Similar relations obtain not only with the other silver halides but also with the closely related silver cyanide and silver thiocyanate.

Since the negative halide sols are readily coagulated by multivalent cations and the positive sols by multivalent anions, the stability of sols is much less if the interacting solutions contain a multivalent ion opposite in charge to the stabilizing ion. Thus a negative sol can be formed by adding 0.05 *N* $AgNO_3$ to 0.05 *N* KI solution, whereas, if barium iodide or cadmium iodide is used, the solutions must be at least as dilute as 0.01 *N* or sol formation does not occur.[50] With different univalent cations, the nature of the cation has little effect; but at higher concentrations, the stabilizing action diminishes in the order: Li, Na, K, NH_4.[51]

The order of stability of the negative sols,[52] stabilized by preferential adsorption of the respective anions from potassium salt in excess, is as follows: AgI > AgBr > AgCl > AgCNS. A similar order obtains for the positive sols prepared with silver nitrate in excess. This order would be deduced from the solubility, indicating that the tendency to precipitate is determined in large measure by the velocity of growth of crystals rather than to agglomeration of particles. Comparing the positive and negative sols, the negative silver iodide is more stable than the positive at all electrolyte concentrations whereas the positive silver chloride sol appears to be more stable than the negative. The greater stability of negative silver iodide sols is evidenced by the following observations: (1) the positive sol is more cloudy and settles out more rapidly than the negative in the presence of a like excess of the stabilizing ions; (2) the positive sol cannot be purified by dialysis without agglomeration, whereas highly pure negative sols can be made in this way; and (3) a freshly precipitated and washed silver iodide gel is peptized in part by shaking with dilute potassium iodide solution, whereas silver nitrate does not peptize such a gel. The marked stability of negative silver iodide was shown by Kruyt and van der

[50] Lottermoser: Kolloid-Z., **2**, suppl. I, p. iv (1907).
[51] Basinski: Roczniki Chem., **14**, 1017 (1934).
[52] *Cf.* Basinski: Kolloid-Beihefte, **36**, 257 (1932).

Williger [53] to be due to the asymmetric position of the zero point of the electrokinetic potential.

To prepare pure concentrated sols of silver iodide, Kruyt and Verwey [54] mixed pure silver nitrate with a 10% excess of potassium iodide, ammonium iodide, or hydriodic acid in such concentrations that the resulting sol contained 80 millimols AgI/l, or less. This was dialyzed at once in an electrodialyzer until quite pure and then concentrated by the process of "electrodecantation" [55] which consists in removing the clear solution from around the cathode membrane, the negatively charged particles having concentrated in the region of the anode membrane. Whether one starts with an iodide or hydriodic acid, the highly purified sol contains only hydriodic acid as stabilizing electrolyte. In this way stable, highly purified sols containing as high as 160 g AgI/kg of sol were prepared.

Sols containing 0.05 g AgI/l were made by electrolysis of 0.001 *N* KI solutions with a silver anode.[56]

Peptization by Ions Other Than Common Ions. Positively charged silver iodide sols are obtained only by adsorption of the common silver ion. Negatively charged sols [53, 57, 58] are formed, however, by the addition of a suitable excess of the following alkali salts: iodide, bromide, chloride, cyanide, thiocyanate, phosphate, ferricyanide, and ferrocyanide; but not by the following: fluoride, nitrate, chlorate, permanganate, formate, carbonate, sulfate, chromate, dichromate, and hydroxide. Since many of the anions in the second list form insoluble silver salts and so should be absorbed, Kruyt concluded that adsorption of an anion is insufficient in itself to form a negative sol; the important thing is that the adsorbed anion should give an isomorphous silver salt in order that the primary double layer which is essential for peptization and stability may form. It appears, however, that the ion need not be exactly isomorphous to effect peptization. For example, alkali chloride and bromide which give cubic silver halides peptize silver iodide which is hexagonal when negative.[4] The important thing is that the adsorbed ion should fit the lattice sufficiently well that it will be taken up by the lattice to a certain extent and so will be distributed in both phases, in other words, will be a potential-determining ion. Whenever ions fit the lattice to a certain extent, it is probable that an

[53] Kruyt and van der Willigen: Z. physik Chem., **A139**, 53 (1928).
[54] Z. physik. Chem., **A167**, 137, 149, 312 (1933).
[55] Pauli: Naturwissenschaften, **20**, 551 (1932).
[56] Peskov and Saprometov: Kolloid-Z., **69**, 181 (1934).
[57] Kruyt and Cysouw: Z. physik. Chem., **A172**, 49 (1935).
[58] Basinski: Kolloid-Beihefte, **36**, 258 (1932).

exchange of lattice ions takes place between the adsorbed ion and iodide ion. This liberates iodide ion from the lattice which may become the predominating potential-determining ion even with isomorphous ions. The failure of Kruyt and Cysouw [57] to detect iodide in the ultrafiltrate from a sol peptized by excess alkali chloride does not mean necessarily that adsorbed iodide ions are not the potential-determining ions. The reversal of charge of a positive silver iodide sol by sodium vanadate [59] is probably caused in part by exchange of vanadate for iodide ions. A fairly large excess of phosphate displaces sufficient iodide ion to peptize the sol. The dispersed particles consist of a mixture of silver iodide with an amount of silver phosphate equivalent to the amount of iodide set free. The addition of a small amount of sodium hydrosulfide to an equivalent mixture of silver nitrate and potassium iodide gives a silver iodide sol and a precipitate of silver sulfide; potassium iodide equivalent to the silver sulfide is the stabilizing electrolyte. Sodium para iodobenzoate behaves like sodium phosphate. A precipitated and thoroughly washed silver iodide is peptized by potassium iodide and cyanide but not by potassium bromide and chloride; the peptizing action of the cyanide results from a reaction with silver iodide giving potassium iodide, the real peptizing agent.

Protected Silver Iodide Sols. Because of the instability of Lottermoser's silver halide sols, Lobry de Bruyn [60] used gelatin and Paal and Voss [61] used sodium lysalbinate as protecting colloids. Paal's preparations are typical hydrophilic colloids, since they are not precipitated even by 5 volumes of saturated sodium chloride or an equal amount of 10% Na_2HPO_4. Gutbier [62] prepared fairly stable sols by treating with the respective halogen a silver sol formed by reduction of silver nitrate with hydrazine hydrate in the presence of gum arabic. Von Weimarn [63] used caoutchouc as protecting colloid in preparing silver halide sols in aromatic hydrocarbons.

Charge and Stability

Thanks to the comprehensive investigations of Verwey and Kruyt,[54, 64] considerable information is available concerning silver iodide sols, especially the aged and dialyzed sols.

[59] Lottermoser and May: Kolloid-Z., **58**, 168 (1932).
[60] Rec. trav chim., **19**, 251 (1900).
[61] Ber., **37**, 3862 (1904)
[62] Kolloid-Z., **4**, 308 (1909).
[63] J. Russ. Phys.-Chem. Soc., **48**, 1046 (1916).
[64] Verwey: Rec. trav. chim., **53**, 933 (1934); *cf., also,* Gorokhovskii and Protass: Z. physik. Chem., **A174**, 122 (1935).

Sols prepared by Lottermoser's method followed by dialysis and concentration by electrodecantation have a very large electrochemical (colloid) equivalent. For a sol with particles having an edge approximately 40 $m\mu$ in length, the particle charge was calculated to be 900 electrons and the "free" charge (from Pauli's conductivity method) 330 electrons per particle as compared with a free charge of 28,000-58,000 electrons per particle for gold sols (Vol. I, p 75). By boiling a pure sol with dilute hydriodic acid followed by dialysis, a sol was obtained having a particle charge of 440 electrons and a free charge of 220 electrons. The colloid equivalent was calculated to be 1500 on the basis of the total charge, and 2700 on the basis of the free charge. It contained 16.7 g AgI/kg of sol; the concentration of hydrogen ion was 0.05 milliequivalent and of the iodide ion 0.00021 milliequivalent per liter; and yet it was quite stable, as we shall see.

From such observations, it follows necessarily that the double layer is not distributed uniformly over the surface but at certain active spots, corners, and edges The number of such active spots and edges is large in a freshly formed precipitate; but, upon aging, the crystals are perfected so that there are fewer places that can take up iodide ions.[65] With excessive aging, the double layer is concentrated in a relatively few spots; hence the colloid equivalent is quite large.

Granting that the primary stability of a sol results from adsorption of potential-determining ions, it is determined by the concentration of these ions and the location of the zero point of the charge. Verwey calculated, for the highly aged sol above, the total potential drop due to free charges ($E - E_0$) from the equation

$$E - E_0 = \frac{RT}{F} \ln \frac{c_0}{c_{I^-}}$$

where c_{I^-} is the iodide ion concentration of the sol ($= 0.00021$ milliequivalent) and c_0 is the iodide ion concentration where $E = E_0$. The latter value is difficult to determine accurately but it is less than 5×10^{-10}; hence $\log c_0/c_{I^-}$ is approximately -3 and $E - E_0 = 0.058 \times -3$ or approximately -0.2 volt. Referring to Fig. 20, it will be seen that the ζ-potential is only about one-third of the total potential drop, the remainder occurring in the silver iodide phase and in the layer of attached ions. The critical value of $E - E_0$ required for the primary stability will thus be almost three times the critical ζ-potential. Since the critical value of ζ is frequently around 40 millivolts the critical value of $E - E_0$ for a dialyzed sol of silver iodide would be

[65] Verwey: Proc. Acad. Sci. Amsterdam, **36**, 225 (1933).

expected to be around -120 millivolts. Actually about -2×0.058 volt was required for the stability. In another highly dialyzed sol in which $c_{I^-} = 10^{-7}$, the value of $E - E_0$ was around -0.150 volt. But since the electrolyte concentration is very small, a considerable portion of this potential drop is the ζ-potential to which the sol owes its stability; hence one may have a stable sol even when the double layer charge is relatively low, provided the electrokinetic potential is above a critical value.

A dialyzed negative silver iodide sol (pAg, about 9) is stable but flocculates when its pAg is raised to about 8 by titrating with very dilute silver nitrate solution. As already noted, the zero point of charge is about $p\text{Ag} = 6$. A positive silver iodide sol coagulates when the concentration of free silver ions is lowered by dialysis to about $p\text{Ag} = 4$.[66] On diluting a positively charged sol with water, the ζ-potential decreases as a result of dilution of the potential-determining silver ion, and finally becomes negative.[53,67] If the sol is diluted with ultrafiltrate from the sol, the ζ-potential decreases to the coagulation point but does not change sign.[68] Gorochovskii[69] found the isoelectric point of silver iodide to depend greatly on the iodide concentration of the sols; but his results are not conclusive since he failed to correct for adsorbed silver or iodide ions on the surface of the silver iodide.

Coagulation by Electrolytes

Comprehensive investigations have been made by Verwey and Kruyt of the phenomena which take place during the coagulation of dialyzed and aged negative silver iodide sols with hydriodic acid the stabilizing electrolyte. The experiments were carried out with various sols and the coagulating power deduced from the tendency to replace hydrogen from the outer portion of the double layer is: $Ce > UO_2 \cong Pb > Ba > H > Cs > K$. As usual, the ion with the higher valence has the higher coagulating and displacing power. Similarly Basinski[70] found the order of coagulating power of cations to be: $Th > Zr$; $Al > Ce > Fe^{+++}$; $Pb > Ba > Cu > Sn > Ca > Ni > Zn > Co > Mn > Mg > Cd$; $Ag > H > NH_4 > K > Na > Li$. Marked

[66] *Cf.* Schneller: Kolloid-Z., **71**, 180 (1935).

[67] *Cf., also,* Lottermoser and Riedel: Kolloid-Z., **51**, 30 (1930).

[68] Basinski: Roczniki Chem., **13**, 117 (1933).

[69] J. Phys. Chem, **39**, 465 (1935); Gorokhovskii and Protass: Z physik. Chem., **A174**, 122 (1935); J. Phys. Chem. (U. S. S. R.), **7**, 354 (1936).

[70] Roczniki Chem., **15**, 430 (1935).

ion antagonism (pp. 216, 322) was observed in the precipitations with mixtures of univalent with bi-, tri-, or tetravalent cations.

The above results were confirmed and extended by Kruyt and van Gils' [71] observations of the effect of electrolytes of varying valence on the mobility of the particles in a silver iodide sol. In Fig. 21 the mobility in microns per second at 1 volt/cm is plotted against the negative logarithm of the electrolyte concentration in mols per liter.

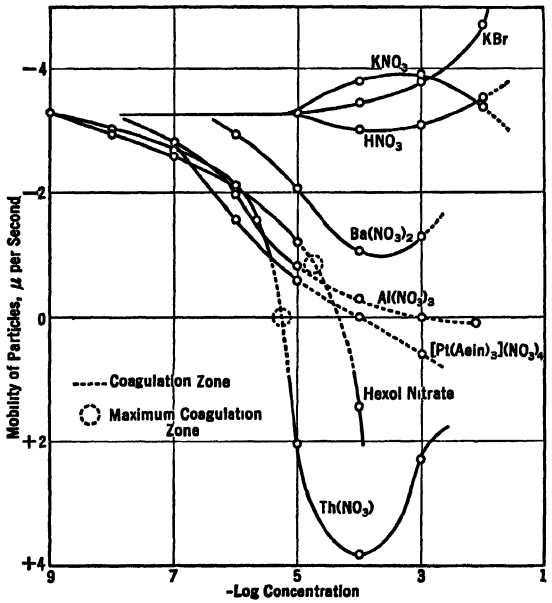


FIG. 21.—Effect of varying concentrations of electrolyte on the mobility of the particles in a silver iodide sol.

The broken portion of the curves marks the zone of instability. The coagulating power of the several cations, as measured by the lowering of the mobility and hence of the ζ-potential to the point of instability, is in the order: Th > [Pt(Aein)$_3$] > Al > hexol > Ba > H > K. Hexol (a hexavalent cobalt amine nitrate) lowers the mobility to zero at a lower concentration than aluminum nitrate. For all salts with multivalent cations, the coagulation of the negative particles takes place at a mobility of approximately 1μ/sec.; but for salts with univalent

[71] Kolloid-Z., **78**, 32 (1937); *cf.* Weiser, Milligan, and Coppoc: J. Phys. Chem., **42** (1938).

cations the critical mobility is much higher (*cf.* Vol. I, pp. 73, 181). Potassium bromide containing the potential-determining bromide ion increases the mobility at all concentrations employed. At sufficiently high concentrations, thorium nitrate and hexol not only reverse the sign of the charge on the particles but even give stable positive sols.

The point of maximum flocculation for thorium nitrate corresponds to zero mobility hence to zero ζ-potential, but for hexol it occurs well above the zero point. The explanation for this is not immediately obvious. In this connection, some observations of Coppoc[71] in the author's laboratory indicate that the zone of instability is quite wide for the concentrated polydisperse sols of silver iodide prepared by the method of Kruyt and Verwey. For example, more than 95% of a typical sol was precipitated in 24 hours by 10 milliequivalents per liter of $BaCl_2$, but 20 milliequivalents per liter were required for complete precipitation in this time.

Titration of Sols. In the coagulation of sols by electrolytes, it has been observed that the ion having a charge opposite to that on the sol is adsorbed in exchange with the counter ions of the double layer on the particles. The adsorption and displacement have been followed potentiometrically in the author's laboratory with a number of hydrous oxide and salt sols during the stepwise addition of electrolytes to the sols. The process has been referred to as "titration of sols." In sols examined by the author (*cf.* pp. 208, 319) only a portion of the counter ions were measurable potentiometrically in the original sol; the remainder were displaced by adding electrolytes and were then measurable. With the aged silver iodide sols of Verwey and Kruyt, the titration procedure was more complicated and less exact. In the first place, the particle charge was much smaller in the iodide sols and the concentration of counter hydrogen ions was correspondingly smaller. Moreover, practically all the counter ions were measurable potentiometrically in the original sol; hence the amount of hydrogen displaced on adding electrolytes was inappreciable. The measurement of hydrogen ion exchanged for the added cation had to be determined in the ultrafiltrate after the addition of the electrolyte. This introduces errors which may be more or less serious depending on the conditions (Vol. II, p. 58).

The procedure was as follows: 15- to 25-cc portions of sol were weighed in a glass-stoppered flask and varying amounts of electrolyte added, followed by reweighing. After 24 hours the uncoagulated samples were ultrafiltered and the coagulated ones were centrifuged and the supernatant solution decanted. The exchanged hydrogen ion

was determined colorimetrically or with the glass electrode. The adsorption of uranium and cerium was estimated directly by colorimetric procedures and that of lead with thorium B as radioactive indicator (p. 50). The exchanged hydrogen ion may serve as an indirect measure of the amount of cation taken up. The results of some observations with a number of different sols are shown graphically in Figs. 22 and 23. From the form of the curves it appears that in certain cases the coagulation point (indicated by an arrow) occurs near the point of maximum adsorption, whereas in others the maximum adsorption is reached well below the coagulation concentration. The latter behavior has not been encountered with sols investigated in the

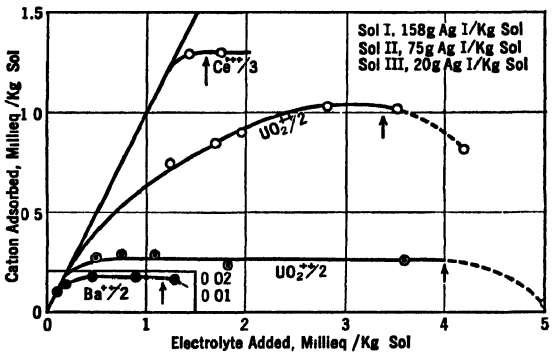


FIG 22.—Adsorption of cations by silver iodide sol.

author's laboratory and calls for special consideration. The barium adsorption estimated indirectly from *p*H measurements on Sol 3 can be disregarded since the change in hydrogen ion concentration is too small to measure accurately. The behavior of Sol 2 with UO_2++ cannot be disposed of in this way, but the possibility of the presence of a stabilizing impurity from the membrane used in the dialysis has not been excluded. In any event the very different behavior of UO_2++ toward Sol 1 and Sol 2 in this respect requires explanation. If contamination of Sol 2 by the membrane is ruled out, another possibility is that the size distribution of the particles in Sol 2 is quite different from that in Sol 1. If most of Sol 2 is coagulated at low concentrations (*cf.* p. 120) but the last trace only at relatively high concentrations (taken as the precipitation value), and if Sol 1 does not exhibit such marked stepwise coagulation, the difference in the behavior of the two sols toward UO_2++ ion is accounted for.[71]

Of special importance are the precise observations of the adsorption of lead ion by a dialyzed sol containing 159 g AgI/kg of sol and the same diluted eleven times (Fig. 23). The dotted line gives the curves for the diluted sol, again on a scale eleven times larger. It is apparent that both curves have the same shape and nearly coincide. The small difference is probably caused: (1) by the giving up of iodide ion from the double layer by dilution, which lowers somewhat the charge on the diluted sol; and (2) by the fact that the dilution is somewhat larger than elevenfold because of the volume occupied by

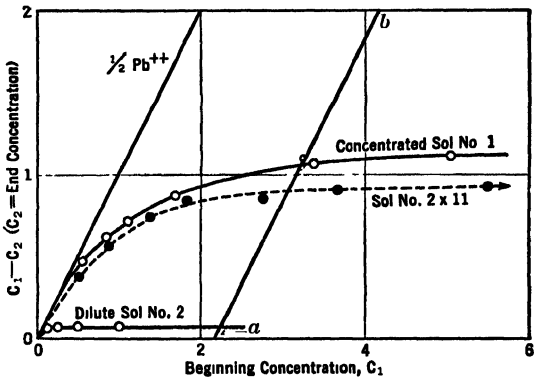


FIG 23.—Adsorption of lead ion by silver iodide sols of two different concentrations.

the particles. These results show that the relative adsorption is independent of the dilution or, what amounts to the same thing, to the mass of the adsorbent. In this case x/m is not a function of c as in the Freundlich isotherm but is a function of c/m, that is, $x/m = f(c/m)$. This same equilibrium applies to the base exchange in clays and permutites (p. 396).

For the concentrated sol (Fig. 23) the coagulation point comes just a little below the point of maximum adsorption. The corresponding point of the curve for the diluted sol represents a concentration of lead eleven times smaller, hence well below the zone of coagulation. The line ab parallel to the straight line $x = y$ connects points of equal concentration of free lead ion. It must be borne in mind that the two sols are alike only in their primary particle size. The secondary aggregates of the original sol are peptized to a greater or lesser extent by dilution, the adsorption equilibria are changed, and the stability toward electrolytes is modified.

Mechanism of the Coagulation by Electrolytes. To effect the coagulation of colloidal particles, the ζ-potential must be lowered below a critical value which allows agglomeration of the particles into aggregates that settle out. This lowering of the ζ-potential is brought about by a contraction of the double layer by adsorption or otherwise. The adsorption mechanism may be represented diagrammatically in Fig. 24. At some active edge or spot a double layer is set up with the

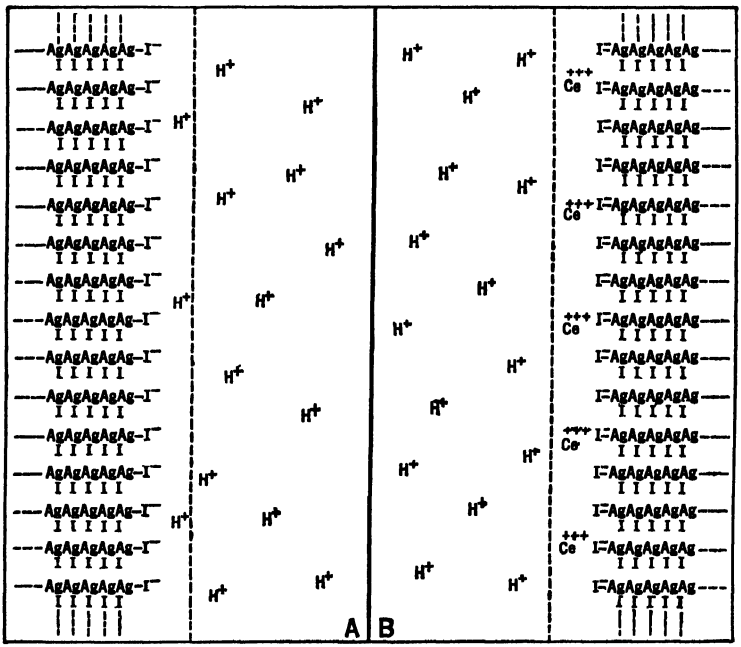


FIG. 24.—Diagrammatic representation of the constitution of a portion of a particle of silver iodide sol (*A*) before and (*B*) after the addition of ceric nitrate.

potential-determining iodide ions constituting the inner layer and hydrogen ions the diffuse outer layer. In the sol under consideration most of the hydrogen ions are measurable potentiometrically in the original sol, but a few shown within the dotted line in Fig. 24*a* are held so strongly by the inner layer that they do not affect the hydrogen electrode. If this particle were ultrafiltered, none of the counter ions would leave the particle entirely and enter the filtrate. On adding an electrolyte such as ceric nitrate, the strongly adsorbed cerium ions dis-

place the hydrogen ion from the innermost portion of the double layer and take up a position closer to the inner layer than the hydrogen ions, Fig. 24*b*. This results in an increase in the hydrogen ion concentration of the sol and, at the same time, in a reduction of the ζ-potential by thinning or contracting the double layer. The displaced hydrogen which causes a decrease in the pH value of the sol is not equivalent to the cerium adsorbed, since most of the hydrogen corresponding to the cerium taken up is measurable in the original sol. On the other hand, if the sol is ultrafiltered at some point below the coagulation value, the increase in the hydrogen ion concentration over that in the ultrafiltrate from the original sol corresponds with the cerium ion adsorbed. The cerium ion has therefore entered into exchange adsorption with the counter hydrogen ion of the original sol; the ζ-potential is lowered by contraction of the double layer as a result of the exchange adsorption or, as Stern[40] would put it, by an increase in the charge of the attached portion of the double layer at the expense of the unattached portion.

Verwey[72] objects to the proposed adsorption mechanism of potential reduction on two grounds: first, he prefers not to refer to exchange adsorption as adsorption; and second, and more important, in certain cases with silver iodide sol, the maximum adsorption, which proved to be about equivalent to the total hydrogen in the double layer, was reached well below the precipitation value, and in other cases, flocculation occurred before sufficient electrolyte was added to reach the maximum adsorption. To account for the maximum adsorption below the precipitation value Verwey accepts in principle Muller's[73] theory of coagulation and concludes that the lowering of the ζ-potential is "merely due to 'compression' of the diffuse outer layer and a subsequent increase in the capacity of this part of the double layer." The essential difference between the point of view of Verwey and that of the author appears to be that the contraction of the double layer or compression of the outer layer is believed by the present author to result from adsorption of precipitating ions whereas Verwey considers that adsorption is neither a necessary nor a sufficient cause of the potential reduction at the surface of the particles. It so happens that in all cases investigated by the author (pp. 207, 318, also Vol. II, pp. 76, 117, 142) adsorption plays the major rôle in bringing about the contraction of the double layer and the consequent lowering of the ζ-potential. It remains to be seen whether the behavior of the sols

[72] Chem. Rev., **16**, 363 (1935).
[73] Kolloid-Beihefte, **26**, 257 (1928).

investigated in the author's laboratory is special and that of silver iodide typifies the general behavior or whether the reverse is true. Certainly the older view of Freundlich that coagulation is the result of neutralization of the charge on the particles by equivalent adsorption is no longer tenable. The important thing is the lowering of the ζ-potential since the charge in the mobile portion of the double layer may be altered without lowering the ζ-potential.[74] The lowering is accomplished by a contraction of the double layer resulting in whole or in part by the precipitating ions being drawn closer (adsorbed) to the attached inner layer. In general, the contraction is greater for ions of varying valence in the order: trivalent > bivalent > univalent which is the same as the usual order of adsorption and displacing power of the ions (p. 205). This means that less of a trivalent ion needs to be adsorbed than of a bivalent ion to lower the ζ-potential to the coagulation point. (*Cf.* Vol. II, p. 77.)

Velocity of Coagulation. Jablczynski[75] studied the velocity of coagulation of silver halide sols both in the presence and the absence of protecting colloids and found the process to take place in accord with Smoluchowski's theory of rapid coagulation (Vol. I, p. 92). This furnishes no evidence as to whether the precipitation is due primarily to aggregation of primary particles or to crystallization, since both processes follow the same law for the determination of number of particles.[2] Schneller[66] showed that, with low concentrations of stabilizing electrolyte, the coagulation is due chiefly to an agglomeration of sol particles and the velocity decreases with progressive coagulation, whereas, with increasing concentrations, the process of recrystallization becomes more and more pronounced and the velocity attains an almost constant value.

In the slow agglomeration process (Vol. I, p. 94) in the presence of a small amount of coagulating electrolyte, the mobility of the particles increases somewhat. Kruyt and de Haan[76] explain this by assuming that the ζ-potential is not lowered uniformly over the surface of the particles. Under these conditions, coalescence takes place at the point of lowest potential, giving agglomerates with a high potential on the outside which may have a higher mobility than the original particles.

The rôle of silver iodide in photographic emulsions will be considered in Chapter VIII.

[74] *Cf.* Bull and Gortner: J. Phys. Chem., **35**, 309 (1931).

[75] Bull. soc. chim., (4) **35**, 1277, 1286 (1924); **39**, 1322 (1926); **43**, 159 (1928); *cf.* Fromherz: Z. physik. Chem., **B1**, 324 (1928).

[76] Kolloid-Z, **51**, 61 (1930).

CHAPTER VII

THE COLLOIDAL HALIDES OF SILVER, LEAD, AND MERCURY

COLLOIDAL SILVER BROMIDE AND CHLORIDE

The general methods of formation and characteristics of gels and sols of silver bromide and chloride are so similar in essential respects to those of silver iodide that the former will not be given the detailed consideration afforded the latter in the preceding chapter. Because of increasing solubility in the order: $AgI < AgBr < AgCl$, the colloidal behavior and stability decrease in the same order; hence silver bromide and chloride have been used much less than silver iodide in the study of colloidal phenomena. In this section it is found convenient to consider the bromide and chloride together. Some reference will also be made to the thallous halides.

. The Precipitated Salts

In the absence of electrolytes that exert an appreciable solvent action the formation of silver halide suspensions takes place in two stages: (1) an initial very rapid formation of primary colloidal particles, and (2) the slower coagulation of the primary particles to give fairly highly dispersed flocculent precipitates. Grain growth by Ostwald ripening and by coalescence of crystals [1] takes place as a secondary process. Greene and Frizzell [2] have studied the two stages in the precipitation of silver chloride [3] by means of a specially designed photronic nephelometer which enabled them to measure the opalescence of the salt suspension from the moment precipitation begins. Visible particles are formed in the initial stage in a few hundredths of a second, and this stage is virtually complete in 2 seconds or less. With increasing concentration of precipitant, the initial opalescence increases

[1] *Cf.* Sheppard and Lambert: Colloid Symposium Monograph, **4**, 281 (1926); **6**, 265 (1928); Kolthoff and Yutzy: J. Am. Chem. Soc., **58**, 1215, 1634 (1937).

[2] J. Am Chem. Soc., **58**, 516 (1936); Greene: **56**, 1269 (1934).

[3] Težak: Bull. soc. chim. roy. Yougoslav., **4**, 137 (1933); Kober: Ind. Eng. Chem., **10**, 556 (1918).

to a maximum and then falls off rapidly. The maximum is reached with a lower concentration of silver nitrate in excess than of hydrochloric acid in excess. Variations in the rate of mixing and the rate of stirring are without measurable influence. The change in opalescence with concentration of reactants is caused by variation in particle size as the concentration of the reagent in excess is increased, the size of the first formed primary particles diminishing in accord with von Weimarn's second law (p. 15). This conclusion is supported by observations with a centrifuge and an ultramicroscope and by measurements of the color of the suspensions and the coagulating effect of nitric acid on them.

The lattices of the fresh precipitates of silver chloride and bromide, like those of silver iodide, have a marked adsorption capacity for many ions, especially dye ions. This is of importance particularly in the photographic process and in the quantitative estimation of the halides using what have been termed adsorption indicators.

Adsorption of Inorganic Ions

Since silver bromide and chloride age rather rapidly, the amount of adsorption per gram of adsorbent is usually rather small. To make accurate estimations of the order of adsorption of common inorganic ions under such conditions, one may use a radioactive indicator such as thorium B and determine the effect of various electrolytes on the adsorption of thorium B. This has been done on silver halide adsorbents, especially silver bromide, by Fajans[4] and Hahn.[5] More recently King and Greene[6] have made a systematic investigation of the effect of alkali and alkaline-earth bromides on the adsorption of thorium B by silver bromide. The salt is negatively charged in contact with bromide ions and will, therefore, adsorb thorium B cations. The amount of this adsorption will decrease in proportion to the nature and amount of other adsorbable cations in the solution. Some results given graphically in Fig. 25 show that the several ions cut down the adsorption of thorium B and are therefore adsorbed in the order: $Cs > Rb > K > Na > Li$, at all concentrations measured. Since all factors including the valence of the cation were held constant except the cation present in the system at equilibrium, there must be some connection between the order of adsorption and some properties of

[4] Fajans and Erdey-Grúz: Z. physik. Chem., **A158**, 97 (1931).

[5] Hahn and Imre: Z. physik. Chem., **A144**, 161 (1929); Imre: **A146**, 41 (1930); Hahn: Z. angew. Chem., **43**, 871 (1930).

[6] J. Phys. Chem, **37**, 1047 (1933); King and Romer: **37**, 663 (1933).

the ions. From Table XI, which gives some properties of the several cations, it appears that the most readily adsorbed ion (1) forms the

TABLE XI

SOME PROPERTIES OF ALKALI IONS

Alkali ion	Adsorption of ThB in % at 8 millimols/l of alkali bromide	Heats of hydration cal./g	Solubilities of bromide at 20° C mols/1000 g H_2O	Ionic size Å
Li	73 3	120	20 9	0 70
Na	70 8	92	8 14	1.00
K	61 0	72	5 69	1 33
Rb	53 8	68	6 95	1.52
Cs	38 7	62	5 78	1.70

most insoluble compound with the opposite ion of the crystal lattice, (2) is the least hydrated, and (3) is the most easily deformable or polarized on forming a compound. These three factors are considered

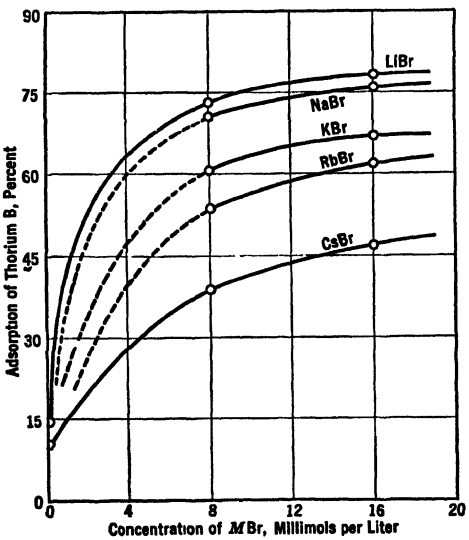


FIG. 25.—Effect of alkali bromides on the adsorption of thorium B by silver bromide.

by Fajans to be of prime importance in determining the adsorption of similar ions.

Experiments similar to the above were carried out by King and Pine [7] to show the effect of various anions and cations on the adsorption of thorium B by thallium bromide and iodide. Contrary to Hahn and Imre's [8] observations, they found that thallium bromide and iodide like silver iodide are always negatively charged in contact with their saturated solutions, and adsorb thorium B. The "neutral powders" obtained by Hahn and Imre must have been precipitated with excess thallium ion and not thoroughly washed. Since the adsorption of various anions will increase the adsorption of thorium B in proportion to their own adsorbability, the following order of adsorption of anions on the thallium salts was obtained: $I > CrO_4 > CNS > Br > PO_4 > Cl > C_2O_4$. This order would be deduced from the solubility of the thallium salts as given in Table XII with the exception of thiocyanate

TABLE XII

ADSORPTION OF ANIONS BY THALLOUS IODIDE

Ion milliequivalents/l	Increase in adsorption of ThB in %	Solubility of the salt millimols/l
I^-	58	0 18
CrO_4^{--}	51	0 57
CNS^-	2	12 0
Br^-	1 9	1 7
PO_4^{---}	0 0	7 0
Cl^-	−5 0	13 0
$C_2O_4^{--}$	−4 0 + but decreasing more rapidly than Cl	53 0

which is again more strongly adsorbed than bromide even though the bromide forms the more insoluble thallium salt (*cf.* p. 107). This may be caused by the greater deformability of the larger complex ion. Cations displace thorium B in the order: $Tl > Ag > Cu > H$.

The adsorption isotherm of cupric ions by silver bromide was determined by Luther,[9] who was investigating the mechanism of the photographic desensitizing action of copper salts. The copper salt

[7] J. Phys. Chem., **37**, 851 (1933).
[8] Z. physik Chem., **A144**, 168 (1929).
[9] Trans. Faraday Soc., **19**, 394 (1923).

was added to a suspension of the silver halide and the adsorption measured by a catalytic method based on the catalytic action of cupric ions on the reaction between persulfate and thiosulfate in the presence of iodide ions. The adsorptive power of the salt after coagulation was less than when suspended. The maximum adsorption of the coagulated compound was approximately 1 mol Cu^{++} per 400 mols AgBr.

Adsorption of Dyes

Studies of the adsorption of dyes on silver bromide and chloride confirm the results previously given for the adsorption on silver iodide (p. 107). For example, Wulff and Seidl [10] found that silver and thallium ions increase the adsorption of the acid dye resorcin in the order: Ag > Tl; and anions cut down the adsorption in the order: Br > Cl > SO_4 > PO_4, CO_3, B_4O_7. The last three ions have little or no effect. The hydrogen ion concentration influences the adsorption of dyes in the usual way, increasing hydrogen ion concentration favoring the adsorption of acid dyes and cutting down the adsorption of basic dyes. Some typical qualitative observations made by Sheppard, Lambert, and Keenan [11] are given in Table XIII. It will be noted that the

TABLE XIII

EFFECT OF *p*H AND OF EXCESS OF COMMON ION ON DYE ADSORPTION

Dye	Nature of dye	*p*H	Adsorption in the presence of	
			Excess Br^-	Excess Ag^+
Pinacynol.	Basic	5 0 7 5	+ + +	+ + −
Dichlorofluorescein . .	Acid	5 0 7 5	− −	+ + +

basic dye pinacynol is adsorbed in an acid medium and in the presence of silver ion. This is attributed by Sheppard to the formation of complex ions; but another explanation is possible (p. 53). In any event, it is a common phenomenon. Thus erythrosin anion is adsorbed

[10] Z. wiss. Phot., **28**, 239 (1930).

[11] J. Phys. Chem., **36**, 174 (1932); Colloid Symposium Monograph, **9**, 174 (1932).

by silver bromide appreciably both in the presence of an excess of silver ion (positive AgBr) and of bromide ion (negative AgBr); on silver iodide, however, the dye anion is adsorbed only when silver ion is in excess. The effects of silver and bromide ions in excess on the adsorption by silver bromide of the acid dye eosin and the basic dye phenosafranin are given graphically in Fig. 26.[4] It is apparent that the adsorption of eosin is very small at the equivalence point but rises sharply with increasing concentration of silver ion; on the other hand,

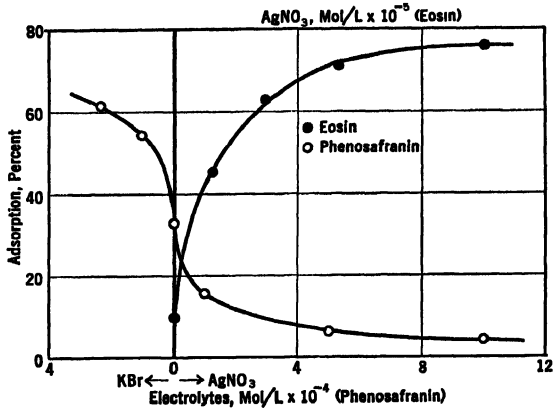


FIG. 26.—Effect of excess silver and bromide ions on the adsorption of dyes by silver bromide. (1) 50 cc eosin containing 10^{-5} mol/l with 1 g AgBr. (2) 15 cc phenosafranin containing 1.6×10^{-5} mol/l with 0.2 g AgBr.

the adsorption of the basic dye increases greatly in the presence of bromide ion and is cut down, but not to zero, in the presence of an appreciable excess of silver ion. The behavior of the basic dye methyl violet is similar to that of phenosafranin.[12]

Quantitative observations of the number of bromide ions required to adsorb one dye ion at saturation are summarized in Table XIV from the results of several investigators. For purposes of comparison, similar adsorption data are given for the inorganic ions thallium and silver. In every instance the adsorption is still far from being a monomolecular adsorption. This is in line with the view that the adsorption is not uniform but takes place only at the more active spots on the surface of the crystals.

[12] Hodakow: Z. physik. Chem., **127**, 43 (1927).

TABLE XIV

ADSORPTION OF DYES ON SILVER BROMIDE

Dye	Ratio at saturation of the surface dye ion : bromide ions	Investigator
Methylene blue in neutral solution	1.8 0	Wulff and Seidl *
Resorcinate in 0 1 *N* NaOH		
0 05 mol/l	1 : 1 7	Wulff and Seidl *
025 mol/l	1 : 2 5	Wulff and Seidl *
.01 mol/l	1 : 1 6	Wulff and Seidl *
Tl^+ in 0 1 *N* NaOH	1 : 3 0	Wulff and Seidl *
Orthochrome T *p*H = 5 5	1 : 2 3	Sheppard and Crouch †
Pinacynol *p*H = 6 8	1 : 1 69	Sheppard, Lambert, and Keenan ‡
Erythrosin	1 : 3 0	Walker, O. J. §
Ag^+	1 : 6 0	Fajans and Frankenburger ‖

* Z. wiss. Phot., **28**, 239 (1930).
† J. Phys. Chem., **32**, 751 (1928).
‡ J. Phys. Chem., **36**, 174 (1932); Colloid Symposium Monograph, **9**, 174 (1931)
§ *Cf.* Fajans and Erdey-Grúz. Z. physik. Chem., **158**, 105 (1930).
‖ Z. Elektrochem., **28**, 499 (1922); Z. physik. Chem., **105**, 273 (1923).

Adsorption Indicators

Definition and Use. Since silver halides, when positively charged by adsorption of silver ions, adsorb and deform certain dye anions strongly, and when negatively charged by adsorption of halide ions adsorb certain dye cations strongly, the dyes even in low concentration give rise to an intensely colored adsorption layer. Fajans[13] and his coworkers have shown that dyes may be employed under suitable conditions as indicators in argentometry. Since the color change at the end point is due to adsorption, Kolthoff[14] called the dyes adsorption indicators. The following experiment demonstrates the principle on which the functioning of an adsorption indicator is based.[15,16] About 3 mg of the sodium salt of eosin is added to a liter of distilled water.

[13] Fajans and Hassel: Z. Elektrochem., **29**, 495 (1923); Fajans and Steiner: Z. physik. Chem., **125**, 309 (1927); Fajans and Wolff: Z. anorg. Chem, **137**, 221 (1924); Hassel: Kolloid-Z., **34**, 304 (1924).

[14] Kolthoff and Furman: "Volumetric Analysis," 111 (1928).

[15] Kolthoff: Chem. Rev., **16**, 87 (1935).

[16] *Cf.* Fajans: "Radio Elements and Isotopes: Chemical Forces and Optical Properties of Substances," 96 (1931).

The salt is dissociated and partly hydrolyzed imparting to the solution a greenish fluorescence and a yellowish red color in transmitted light. The addition of 2 cc of 0.1 *N* $AgNO_3$ causes no appreciable color change since the solubility product of silver eosinate is not exceeded. On adding 0.5 cc of 0.1 *N* alkali bromide, an intense color change to red or red-violet occurs and the fluorescence disappears. The highly dispersed silver bromide adsorbs silver ions and, simultaneously, an equivalent amount of eosin ions which are deformed, the process causing a marked change in color. On further addition of bromide, more silver bromide results and the color deepens until the equivalence point is passed, whereupon the excess bromide ions displace the adsorbed eosin ions which return to the solution. The silver bromide particles are decolorized thereby and the solution takes on its original color and fluorescence. The color change is completely reversible.

If a basic dye such as Rhodamine 6G is substituted for eosin, the process is the reverse of the above. In the presence of excess silver ions, these are adsorbed primarily and prevent the adsorption of the dye cation; but as soon as a slight excess of bromide is present, the latter ions are adsorbed and attract an equivalent amount of dye cations which give an intense red color to the silver bromide suspension.

Mechanisms of the Action of Adsorption Indicators. Fajans' interpretation of the mechanism of the action follows from the above experiments: A dye anion is not adsorbed by a silver halide as long as an excess of halide ions is present in the supernatant solution; with a slight excess of silver ions part of the latter are adsorbed which results in an equivalent adsorption of the dye anions. The reverse process takes place with a dye cation as adsorption indicator. The adsorption usually causes deformation of the dye ion with an intense color change which marks the equivalence point. It is not essential that a color change occur at the end point. When the indicator is unadsorbed, the supernatant solution has the color of the dissolved dye and the precipitate is white (AgCl) or yellowish (AgBr and AgI); when strong adsorption of the dye takes place, the solution is decolorized and the precipitate takes on the color of the dye. Taking advantage of these facts Berry and Durrant[17] used tartrazin as an indicator in titrating silver with bromide or chloride, and Lang and Messinger[18] used diphenylamine blue to titrate strongly acid chloride with silver nitrate, under suitable conditions.

[17] Analyst, **55**, 613 (1930).
[18] Ber, **63B**, 1429 (1930).

According to Fajans' mechanism, a dye anion is adsorbed as a secondary process following the primary adsorption of silver ion, and a dye cation is adsorbed as a secondary process following the primary adsorption of halide ion on the silver halide surface. If this were strictly true, a dye anion should not be adsorbed in the presence of excess halide ion and a dye cation should not be adsorbed in the presence of excess silver ion. As a matter of fact, acid dyes are frequently adsorbed to some extent even in the presence of excess halide and basic dyes in the presence of excess silver. Eosin, for example, is useless as an adsorption indicator in the titration of chloride since the dye ion is adsorbed by silver chloride from the beginning of the titration in spite of the presence of excess chloride ions; hence the end point is not sharp in titrating chloride. On the other hand, it is entirely satisfactory in titrating bromide and iodide. Similarly, erythrosin may not be used as an indicator in titrating silver, chloride, or bromide but is satisfactory in titrating iodide. The adsorption of phenosafranine and methyl violet in the presence of both excess silver and excess bromide has been considered above (p. 131). In spite of this behavior, phenosafranine is a good adsorption indicator in titrating silver with bromide; and methyl violet may be used in titrating silver with chloride. The essential thing is that the dye anion should not be adsorbed very strongly in the presence of ions of the same sign but should be highly adsorbed in the presence of a slight excess of ions of opposite sign, in order that a marked color change may result at or near the equivalence point.

It has been generally assumed that the adsorption of dye ions in the presence of lattice ions of the same sign is due to a primary adsorption of both the lattice and the dye ions. Kolthoff[19] claims, however, that the adsorption of dye ions under these conditions is wholly or in part an exchange adsorption between the dye ion and the lattice ion at the surface of the particles, just as was claimed for the adsorption of dyes by lead and barium sulfate (p. 32). For example, if silver chloride containing neither an excess of adsorbed silver nor adsorbed chloride (equivalent body) is shaken with fluorescein, a slight adsorption of the dye anion (Fln^-) takes place and an equivalent amount of chloride appears in solution. This may be represented by the replacement equation:

$$\underset{\text{Surface}}{Ag^+Cl^-} + \underset{\text{Solution}}{Fln^-} \rightleftarrows \underset{\text{Surface (reddish)}}{Ag^+Fln^-} + \underset{\text{Solution}}{Cl^-}$$

[19] Kolthoff: Kolloid-Z., **68**, 190 (1934); Chem. Rev., **16**, 87 (1935); *cf.* Kolthoff and Yutzy: J. Am. Chem. Soc., **59**, 1215, 1634 (1937).

In this instance the replacement of chloride by fluorescein is slight; but to quote Kolthoff: "in the presence of a slight excess of silver, however, the chloride ion concentration decreases sharply, favoring a marked replacement of chloride ions in the surface by dye ions, resulting in a reddish color of the precipitate." It is apparent that Kolthoff considers the dye adsorption in any event to be an exchange adsorption between the dye ions and the lattice ions. With eosin (Eos^-) and silver chloride the exchange is represented by the equation:

$$\underset{\text{Surface}}{Ag^+Cl^-} + \underset{\text{Solution}}{Eos^-} \rightleftarrows \underset{\substack{\text{Surface}\\(\text{red})}}{Ag^+Eos^-} + \underset{\text{Solution}}{Cl^-}$$

As we have seen, the action takes place to such an extent, even in the presence of excess chloride, that the dye is useless as an adsorption indicator for chloride titration. With bromide and iodide, on the other hand, this effect is not sufficiently pronounced to interfere with the titration.

In titrating silver with bromide using the basic dye phenosafranine ($Phen^+$) as indicator, the following exchange adsorption of lattice ions is assumed:

$$\underset{\text{Surface}}{Ag^+Br^-} + \underset{\text{Solution}}{Phen^+} \rightleftarrows \underset{\substack{\text{Surface}\\(\text{red})}}{Phen^+Br^-} + \underset{\text{Solution}}{Ag^+}$$

And in titrating chloride and bromide with mercurous nitrate using bromphenol blue ($Bp\ B^-$), it is believed to be:[20]

$$Hg_2Cl_2 + 2Bp\ B^- \rightleftarrows Hg_2(Bp\ B)_2 + 2Cl^-$$

Although Kolthoff has demonstrated the existence of what appears to be an exchange of lattice ions in the adsorption of dyes on the silver halides, he seems to have taken an extreme position in claiming that, under the conditions specified, the dye adsorption is essentially an exchange adsorption between dye ions and the surface lattice ions. In the presence of excess silver nitrate, a silver halide adsorbs silver ions preferentially, nitrate ions being the counter ions in the diffuse outer layer. If a dye such as fluorescein is present under these conditions it seems altogether probable that most if not all the adsorption is the result of an exchange between the dye anion and the counter nitrate ions. A similar view seems to be held by Verwey,[21] who says

[20] Kolthoff and Larson: J. Am. Chem. Soc., **56**, 1881 (1934).
[21] Kolloid-Z., **72**, 187 (1935).

that the action of adsorption indicators rests fundamentally on an exchange of counter ions, a phenomenon which always takes place when counter ions of the right sign are in the double layer. He believes further that a pure or direct adsorption of the dye ion can take place which complicates the relations in the double layer. This pure adsorption can be mistaken for a lattice ion exchange which, in favorable cases, corresponds almost exactly with it. Whenever this pure adsorption (or lattice ion exchange adsorption) is large in comparison with the counter ion exchange adsorption, the dye cannot be used as indicator.

In any titration it is important to get the color change at the equivalence point. As Verwey points out, if an adsorption indicator is used which enters into counter ion exchange only, with no direct adsorption on the precipitate, the color change should take place exactly at the isoelectric point; if some direct adsorption comes in, the change will take place on one side or the other of the isoelectric point. It follows from this that silver iodide with isoelectric point of $p\mathrm{Ag} = 6$ is titrated with greatest exactness using a suitable dye cation rather than anion as indicator, since a weak adsorption of the former will shove the isoelectric point more nearly to the equivalence point.

Applicability of Adsorption Indicators. Even when a suitable indicator is found for a given titration, various factors must be taken into account for its successful application.[15] Since the adsorption of the indicator is confined to the surface of the precipitate, the method is applicable, in general, only when the surface is large. The silver halides age very rapidly after flocculation thereby decreasing the total surface of the precipitate; hence the titration is less exact in the presence of electrolytes which induce flocculation of the halide sol much before the end point. For this reason an excess of acid will interfere with the detection of the end point. Furthermore, hydrogen ions may exert a specific effect on the indicator. Fluorescein, for example, is a weak acid, similar in this respect to phenolphthalein, and hydrogen ions will remove the indicator ions by driving back the dissociation of the dye. Fluorescein must therefore be used in neutral solution. Dyes such as eosin, diiodofluorescein, bromphenol red, metanil yellow, etc., will work in weakly acid solution, and dichlorofluorescein may be used in titrating chloride at a $p\mathrm{H}$ smaller than 4.[22]

The concentration of the solution to be titrated is important in determining the applicability of an indicator. Bromides and iodides can be titrated with eosin as indicator in solutions even more dilute than

[22] Kolthoff, Lauer, and Sunde: J. Am. Chem. Soc., **51**, 3273 (1929).

0.001 *N*. Chlorides cannot be titrated with fluorescein as indicator at dilutions greater than 0.005 *N* since the more soluble silver chloride tends to separate in a coarser form than the bromide or iodide. Moreover, the adsorbability of fluorescein is much less than that of chloride. Dichlorofluorescein is so much more strongly adsorbed than fluorescein that it may be used in titrating chloride solutions as dilute as 0.001 *N*.

Under proper conditions it is possible to determine an ion in the presence of another which also yields a slightly soluble salt with the reagent. Thus Fajans and Wolff [23] titrated iodide in the presence of chloride with diiodofluorescein, dimethyl diiodofluorescein, and rose bengal as indicators; and Kolthoff estimated small amounts of iodide in the presence of much chloride by adding ammonium carbonate and using eosin as adsorption indicator.

The application of adsorption indicators in quantitative analysis is confined chiefly to the titration of halides with silver or mercurous mercury, or the reverse. In qualitative analysis the adsorption-indicator principle is used in the colorimetric detection of several metals, for example: magnesium with titan yellow; beryllium with curcumin and 1,2,5,8-oxyanthraquinone; and aluminum, with the latter reagent and with alizarin, purpurin, and aurintricarboxylic acid.

Hydrosols

Like the corresponding silver iodide sols the negative sols of silver bromide, chloride, and thiocyanate formed in the presence of a slight excess of the respective anions are more stable than the positive sols formed in the presence of excess silver ions. Wereide [24] describes the preparation of dilute silver halide sols by electrolysis of the corresponding acid using silver electrodes and either alternating or direct current. Stable sols may be prepared by precipitating in the presence of gelatin [25] or gum arabic.[26] It is of interest in this connection, that concentrated chloride solutions can be titrated quite accurately by Mohr's method using chromate as indicator, provided 5–10 cc of 0.1% agar is added to the chloride solution before adding the silver ion. The effect of the agar is to prevent the balling up of the casein-like precipitate and thus to give a much sharper end point.[27]

[23] Z anorg. Chem, **137**, 221 (1924).
[24] Z. Physik., **41**, 864 (1927).
[25] Chatterji and Dhar: J. Indian Chem. Soc., **7**, 177 (1930).
[26] Van der Wielen and Witteboon: Pharm. Weekblad, **72**, 1037 (1935).
[27] Lottermoser and Lorenz: Kolloid-Z., **68**, 201 (1934).

The results of the work of Jablczynski and coworkers[28] and of Schneller[29] on the kinetics of the coagulation of silver halide was considered in part in the silver iodide chapter (p. 125).

Because of the opalescence imparted to water in which a small amount of silver halide is suspended, very small amounts of silver[30] or of chloride[31] have been determined by nephelometric titration to the so-called "equal opalescence" end point. This is an important operation in precise atomic-weight measurements where the stoichiometric ratio is determined between a pure compound furnishing chloride or bromide ions and pure silver. Johnson[32] has investigated in detail the effect on the equal opalescence end point of various factors such as the order of titration, the presence of extra compounds in the solution, shaking and cooling, etc. In general, it was found that under the proper conditions the method meets the accuracy demanded in atomic-weight investigations provided shaking and cooling of the analytical systems are avoided. These operations in the presence of a variety of foreign compounds tend to leave in the supernatant liquid an excess of chloride equivalent to several tenths of a milligram per liter. Whether this is real or virtual, the effect represents a source of constant error which, if permitted to operate in an atomic-weight titration, would tend to give a low value for the calculated atomic weight. The fluctuations in the observed results may be ascribed to some combination of the following factors: adsorption of ions by silver chloride during peptization and coagulation; adsorption on the precipitate; differences in the coagulating action of the two precipitating agents; the peptizing and coagulating action of the foreign compound.

THE COLLOIDAL HALIDES OF LEAD

With the exception of the fluoride, the halides of lead are much more soluble than the corresponding halides of silver and so are less

[28] Bull. soc. chim., (4) **33**, 1392 (1923); **35**, 1277, 1286 (1924); **39**, 1322 (1926); **43**, 159 (1928); **47**, 50 (1930).

[29] Kolloid-Z., **71**, 180 (1935); *cf.* Jablczynski and Jaszczolt: Roczniki Chem., **9**, 111 (1929).

[30] Richards and Wells: Am. Chem. J., **31**, 235 (1904); Wells: **35**, 99 (1906); Richards: **35**, 510 (1906).

[31] Lamb, Carlton, and Meldrum: J. Am. Chem. Soc., **42**, 259 (1920); Kolthoff and Yutzy: **55**, 1915 (1933).

[32] J. Phys. Chem., **35**, 540, 830, 2237, 2581 (1931); **36**, 1942 (1932); **39**, 781 (1935); Johnson and Low: **36**, 2390 (1932); *cf.* Briscoe, Kikuchi, and Peel: Proc. Roy. Soc. (London), **133A**, 440 (1932); Scott and Hurley: J. Am. Chem. Soc., **59**, 1297 (1937).

readily obtained in the colloidal state. The solubilities in millimols per liter at 25.2° are: $PbCl_2$, 38.80; $PbBr_2$, 26.28; and PbI_2, 1.58.[33] From the von Weimarn theory one would not expect any of these salts to be thrown down in the colloidal state from aqueous solution. Actually the most soluble lead halide, the chloride, precipitates as a slimy mass which runs through a fine-pored filter paper, when a molar solution of sugar of lead is mixed with a 2 *M* solution of sodium chloride.[34] In a systematic investigation with the three lead halides, von Weimarn found that the size of the precipitated particles varies inversely as the solubility when the precipitation takes place under the same conditions of supersaturation.[35]

Although unprotected hydrosols are quite instable, von Weimarn obtained fairly stable sols in aqueous alcohol by carrying out the precipitation preferably in the presence of an excess of lead ions. As would be expected the stability of the aqueous alcosols follows the order of decreasing solubility in water: $PbI_2 > PbBr_2 > PbCl_2$.

Stable hydrosols of lead iodide are obtained with the aid of gelatin as protecting colloid.[36] Reinders[37] mixed 10 cc each of 0.1 *N* $Pb(C_2H_3O_2)_2$ and KI with 80 cc of 0.05% gelatin and obtained an orange-yellow sol with a beautiful silky luster. The particles were hexagonal plates which exhibited a distinct double refraction when examined with crossed nicols. With 0.3% gelatin, the sol formed more slowly and the particles were much finer; but after some weeks the gradual growth of the crystals caused precipitation of the sol. This sedimentation may be prevented almost entirely by using sodium "protalbinate" as the protecting colloid:[38] 5 cc of a 5% solution of this protector were heated with 15 g of a 20% solution of $Pb(C_2H_3O_2)_2$. The resulting lead "salt" was dissolved in sodium hydroxide and treated with potassium iodide giving a sol which is reddish brown in transmitted light and greenish yellow in reflected light. After purification by dialysis, the preparation may be evaporated to dryness without destroying the sol-forming property of the residue.

Conductivity measurements on mixtures of lead acetate and potassium iodide in the presence of agar show that the agar keeps the lead iodide in a supersaturated solution and inhibits greatly the precipita-

[33] Von Ende: Z. anorg. Chem., **26**, 159 (1901).

[34] Van der Velde: Chem.-Ztg, **17**, 1908 (1893).

[35] Von Weimarn, Chên, Kida, and Yasuda: Kolloid-Z., **42**, 305 (1927).

[36] Lobry de Bruyn: Z. physik. Chem, **29**, 562 (1899).

[37] Kolloid-Z., **21**, 164 (1917); *cf.* Lachs: J. phys. radium, **3**, 125 (1922).

[38] Leuze: "Zur Kenntnis kolloidaler Metalle und ihrer Verbindungen," 32 (1904).

tion of the salt[39] (p. 89). That sol formation is prevented is evidenced by the absence of a color change on mixing the solutions. The precipitation of lead iodide in agar gels is likewise slowed down and the form of the crystals is influenced by the purity of the agar. Large, beautifully formed crystals are obtained by allowing a potassium iodide solution to diffuse slowly into a silica gel containing lead acetate.[40] Rhythmic bands result in silica gel in the presence of citric or tartaric acids which decrease the grain size of the iodide.[41]

THE COLLOIDAL HALIDES OF MERCURY

Mercurous Halides

The precipitates formed on mixing the respective alkali halides with mercurous nitrate are fine crystalline powders. These salts have been used by Hahn and Imre[5] in conjunction with the corresponding silver salts, in their investigations of the mechanism of the adsorption process at ion lattices (p. 109).

Stable hydrosols of mercurous halides have been prepared only in the presence of protecting colloids. On mixing 0.05 *M* solutions of NaCl and slightly acidified $HgNO_3$, strongly double refracting needle-crystals of mercurous chloride, 10μ in length, are formed. In the presence of 0.3% gelatin, the growth of the crystals is inhibited to such an extent that a stable sol results which is milky bluish-white in reflected light and exhibits distinct double refraction when examined with crossed nicols.[42]

If a dilute solution of a mercurous salt is treated with a stannous salt, a sol is formed consisting of hydrous stannic oxide with adsorbed mercury. Such a sol is converted into a mercurous halide sol stabilized by stannic oxide, by treating with the amount of halogen corresponding to the reaction $2Hg + X_2 \rightarrow 2HgX$ or with the amount of mercuric salt corresponding to the reaction $Hg + HgX_2 \rightarrow 2HgX$.[43] Very stable mercurous halide sols are prepared for therapeutic use by the interaction of a mercurous salt and alkali halide in the presence of albuminous bodies, followed by dialysis.[44] By careful evaporation of

[39] Bolam: Trans. Faraday Soc., **24**, 463 (1928); **26**, 133 (1930).

[40] Holmes: J. Phys. Chem., **21**, 718 (1917); J. Franklin Inst., **184**, 758 (1917).

[41] Isemura: J. Chem Soc., Japan, **58**, 58 (1937).

[42] Reinders: Kolloid-Z., **21**, 165 (1917).

[43] Lottermoser: J. prakt. Chem., (2) **57**, 485 (1898).

[44] Galerosky: Pharm. Ztg., 230 (1904); Chemische Fabrik von Hayden: Chem. Zentr., II, 1757 (1905).

the sol or by coagulation with alcohol, a gel results which is peptized by water, alcohol, ether, or benzene. The gel thrown down by an acid is repeptized by thorough washing with water containing a little alkali. Any germicidal or fungicidal action of mercurous halide sols is undoubtedly due primarily to the ions present and not to the colloidal particles.[45]

Mercuric Halides

Mercuric chloride and bromide are too soluble to form hydrosols but a fairly stable iodide sol might result in the presence of a suitable protecting colloid. Charitschkov [46] made mercuric chloride sols by the action of hydrogen chloride on a solution of mercuric "naphthenate" in benzene, toluene, or light petroleum.

The transition rhombic HgI (yellow) $\rightleftarrows$ octahedral HgI (red) is of interest especially in connection with the effect of protecting colloids on the process. The transition temperature for small crystals is usually given as 127°, but Cohen and Bredée [47] place it at 125.1 to 128.4°. Kohlschutter [48] showed that the transition from the red to the yellow form was sharp at 129–130°, using large single crystals. At room temperature the yellow form, prepared by subliming the red at a low pressure or in a stream of indifferent gas, changes slowly from lemon yellow to bright yellow and then to red, the change being more rapid for large crystals than for small. The transformation was found to be autocatalytic in both directions.[49]

On mixing solutions of mercuric chloride and potassium iodide at room temperature, the yellow form, identical with that obtained by heating the red,[50] appears first; but this goes over promptly to the stable red modification. If gelatin [51] is added to the solutions before mixing, the yellow form is stabilized probably by an adsorbed film of gelatin on the surface, and goes over only very slowly into the red. Egg albumin has a similar action, but agar has little or no effect in inhibiting the transformation, indicating that agar is not adsorbed strongly by mercuric iodide. The change from the red to the yellow

[45] Wedekind and Bruch: Biochem. Z, **208**, 279 (1929).
[46] J Russ. Phys.-Chem. Soc., **52**, 97 (1920); **122** (2), 827 (1922)
[47] Z. physik. Chem, Bodenstein Festband, 481 (1931).
[48] Kolloid-Beihefte, **24**, 319 (1927); *cf.* Coppock: Nature, **133**, 570 (1934).
[49] Benton and Cool· J. Phys. Chem, **35**, 1762 (1931).
[50] Jolibois and Fouretier: Compt. rend., **197**, 1322 (1933).
[51] Friend: Nature, **109**, 341 (1922); Sameshima and Suzuki: Bull. Chem. Soc., Japan, **1**, 81 (1926); Sameshima: **3**, 189 (1928); Kisch: Kolloid-Z., **49**, 433 (1929).

form is likewise inhibited by the presence of gelatin, a temperature well above the ordinary transition point being necessary to effect the transformation.

The yellow form of the iodide which precipitates first from an alcoholic solution starts to go over to the red form within 15 minutes. The transformation begins at an edge of the crystal and spreads parallel thereto to the opposite edge.[52]

[52] Coppock: Nature, **133**, 570 (1934).

CHAPTER VIII

THE SILVER HALIDES IN PHOTOGRAPHY

Photochemical Decomposition of Silver Halides

Cause of the Darkening

The darkening of silver chloride in the light was probably discovered by Schulze in 1727. Scheele[1] likewise observed it and was the first to show that chlorine is liberated in the process and that violet rays are more effective than red or green rays in producing the phenomenon. The darkening is caused by the liberation of finely divided metallic silver which colors the salt violet to brown to black. The photochemical decomposition with the accompanying discoloration is superficial; hence the loss in weight due to vaporization of the halogen liberated with the silver is slight when the halide is insolated in mass.[2] By the aid of a microbalance Hartung[3] showed that thin films of the halides are almost completely decomposed into silver and the halogen on prolonged exposure to sunlight. Thus it was found that more than 96% of the bromine was expelled by insolating thin films of silver bromide in a vessel containing a suitable halogen absorbent, which was evacuated to 0.001 mm before sealing. Under similar conditions, 83% of the iodine was expelled from silver iodide and 91% of the chlorine from silver chloride. If the vessel was filled with hydrogen instead of air before evacuating, the percentage of chlorine expelled from silver chloride was 95, and that of iodine from silver iodide, 92. Hartung showed conclusively that the decomposition products are always silver and the halogen;[4] there is no indication of the formation of a sub-halide.

[1] *Cf.* Mellor: "Comprehensive Treatise on Inorganic and Physical Chemistry," **3**, 391 (1923).

[2] *Cf.* Baker: J. Chem. Soc., **61**, 728 (1892); Richardson: **59**, 536 (1891); Koch and Schrader: Z. Physik, **6**, 127 (1921).

[3] Phil. Mag., (6) **43**, 1056 (1922); J. Chem. Soc., **121**, 682 (1922); **127**, 2691 (1923); **129**, 1349 (1926).

[4] *Cf.* Koch and Kreiss: Z. Physik, **32**, 384 (1925); Ehlers and Koch: **3**, 169 (1920).

In this connection attention should be called to the existence of an optimum concentration at which chlorine attacks silver most readily, the rate of chlorination decreasing rapidly as the concentration of halogen in the surrounding air increases. This recalls the behavior of phosphorus, which is not attacked by pure oxygen at room temperature probably owing to the formation of a thin protecting film of oxide.[5]

Mechanism of the Process

Sheppard and Trivelli[6] and Fajans,[7] at about the same time and independently, proposed the following reaction scheme to represent the primary photochemical change in the production of the latent image (p. 153), where θ represents an electron:

(*a*) $\quad Br^- - \theta = Br$ (bromine atom)

(*b*) $\quad Ag^+ + \theta = Ag$ (silver atom)

Eggert and Noddack[8] first investigated the photochemical decomposition of silver halide with the purpose of determining whether Einstein's photochemical equivalence principle is applicable. From the results of their observations it was concluded that the primary reaction agrees with this principle in the sense that, for each quantum of light absorbed, one silver atom is produced, thus:

(*a*) $\quad Br^- + h\nu = Br + \theta$

(*b*) $\quad Ag^+ + \theta = Ag$

Eggert and Noddack's experiments were carried out with gelatin-silver bromide plates, the gelatin in which was supposed to absorb most of the shorter waves. Weigert[9] claims that this is not the case and that Eggert and Noddack's conclusions are therefore not justified. More recently, however, the applicability of the photochemical equivalence principle has been verified by Hilsch and Pohl[10] and by Feldman and

[5] *Cf.* Weiser and Garrison: J Phys. Chem., **25**, 61, 349, 473 (1921).

[6] Phot. J., **61**, 403 (1921); Sheppard and Vanselow: J. Phys. Chem, **33**, 331 (1929).

[7] Fajans and Beckerath: Chem-Ztg., **45**, 666 (1921); Fajans and Frankenburger: Z. Elektrochem., **28**, 499 (1922).

[8] Sitzber. preuss. Akad. Wiss., **31**, 631 (1921).

[9] Z physik. Chem, **99**, 499 (1921); Z. Physik, **18**, 232 (1923).

[10] Z. Physik, **64**, 612 (1930).

Stern [11] with the silver halides in the absence of gelatin. Some results are summarized in Table XV in which $N_{AgBr}/\Delta Q$ is the quotient obtained by dividing the entire number of molecules of AgBr present, N_{AgBr}, by the number of absorbed quanta ΔQ; and ϕ, the quantum yield, is given by $\Delta N/\Delta Q$, where ΔN is the number of halogen ions

TABLE XV

QUANTUM YIELD IN THE PHOTOCHEMICAL DECOMPOSITION OF SILVER HALIDES

Preparation	Wave length of light mμ	$\frac{N_{AgBr}}{\Delta Q}$	$\phi = \frac{\Delta N}{\Delta Q}$	Investigator
Photographic plate	436	5×10^3	Approx. 1	Eggert and Noddack
AgBr (crystals)	475	4×10^7	Approx 1	Hilsch and Pohl
AgCl (crystals)	405			
AgBr (precipitated)*	436	1×10^6	1	Feldman and Stern
AgBr (crystals)	365	2×10^5	0 4	Feldman and Stern

* Suspended in a dilute solution of $NaNO_2$ as halogen acceptor.

set free and ΔQ has the same significance as above. From these and similar data Feldman and Stern conclude that the quantum yield in the decomposition of silver chloride and bromide with sodium nitrite solution as halogen acceptor is unity [12] within the limits of experimental error (less than 10%); and that the quantum yield in the formation of the latent image on the photographic plate is probably in the neighborhood of unity.[13] This does not mean that the whole process of electron transfer is as simple as the above equations would indicate.[14]

Optical Sensitization

Silver halides are normally photosensitive only in their absorption region in the blue violet. This sensitivity can be increased, however, by various processes of what has been termed optical sensitization. The

[11] Z. physik. Chem., **B12**, 449, 467 (1931); **B26**, 45 (1934); *cf.* Plotnikov: Phot Korr, **67**, 199 (1931).

[12] *Cf.* Mutter: Z. wiss. Phot, **26**, 193 (1929).

[13] *With x-rays, each absorbed quantum appears to liberate approximately 1000 atoms of silver.* Eggert and Noddack: Z. Physik, **43**, 222 (1927); **31**, 796 (1925)

[14] *Cf.* Sheppard and Vanselow: J. Phys. Chem, **33**, 250 (1929).

best known optical sensitizers are certain dyes that sensitize the silver halide for an extended spectral region which is not the same as the absorption spectrum of the dye in ordinary solvents but which is probably identical with the absorption of the dye-silver halide combination.[15] Other optical sensitizers are: adsorbed silver ion, colloidal silver, and silver sulfide. Because of the colloidal behavior involved, the mechanism of the optical sensitization process will be considered in some detail.

Sensitization by Adsorbed Silver Ion. In 1863 Vogel[16] called attention to the fact that silver bromide precipitated in the presence of excess silver ions changes color in light much more rapidly and strongly than the salt formed in the presence of excess bromide ions. The classical explanation of this action is that silver nitrate acts as a bromine acceptor which removes the bromine liberated by the light in amount equivalent to the silver, in accord with the equation: $AgNO_3 + Br_2 + H_2O \rightarrow AgBr + HOBr + HNO_3$. By removing bromine, the recombination with silver is prevented; hence the photochemical decomposition proceeds faster and further in the presence of the acceptor. This explanation doubtless holds in part, but Fajans and coworkers[17] suggest that silver nitrate not only acts as a bromine acceptor but in some way influences the primary light process also. An effect of adsorbed ions on the primary light process appears to be the only way of accounting for the marked increase in photochemical sensitivity of zinc sulfide in the presence of zinc chloride[18] (p. 288).

To test his theory Fajans[19] determined the absorption curve for samples of silver bromide in contact with silver and bromide ions respectively. Since, in accordance with the Grotthus-Dreaper law, light is photochemically active only when it is absorbed, it follows that every influence which affects the primary photochemical process would alter the absorption curve. Some actual observations of the absorption on carefully prepared silver bromide-gelatin emulsions are shown graphically in Fig. 27, from which it is apparent that the silver body absorbs light much more strongly than the bromide body. Adsorbed thallium ions likewise increase the light absorption.

[15] *Cf.* Sheppard: Chem. Rev., **4**, 319 (1927).

[16] Pogg. Ann., **119**, 497 (1863).

[17] Fajans and Beckerath: Z. physik. Chem., **97**, 478 (1921); Fajans and Frankenburger: **105**, 255 (1923); Z. Elektrochem., **28**, 499 (1922).

[18] Weiser and Garrison: J. Phys. Chem., **31**, 1242 (1927).

[19] Fajans, Fromherz, and Karagunis: Z. Elektrochem., **33**, 548 (1927); Fromherz: Z. physik. Chem., **B1**, 324; Fromherz and Karagunis: 345 (1928).

An absorption band for solid substances exhibits a maximum and two branches that fall more or less steeply toward longer and shorter wave lengths respectively. In the case of silver bromide it was possible to study only the branch descending to longer wave lengths, and the curves of Fig. 27 do not show whether the observed effect indicates a raising of the whole band, in other words an increase of the absorption over the whole spectrum, or a shifting of bands toward the longer wave lengths, or a combination of the two.

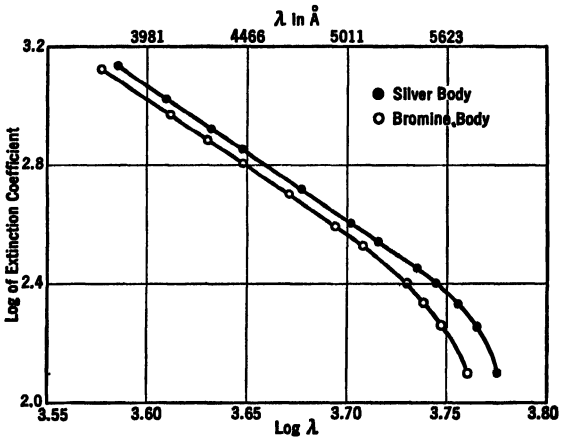


FIG. 27.—Influence of the adsorption of silver and bromide ions on the absorption of light by silver bromide sol.

The energy ϵ of a quantum transferred to a single molecule, ion, or atom stands in the following relation to the wave length λ, the frequency ν, and the velocity of light c

$$\epsilon = h\nu = h\frac{c}{\lambda}$$

The absorption of light of shorter wave length may thus cause the greater chemical change; but the number of absorbed quanta, that is, the amount of absorbed light and hence the number of photochemically altered particles, is also of importance in determining the course of the photochemical change. If the observed effect of the adsorbed silver ions in the case at hand consists in raising the whole absorption band, this would indicate that the amount of absorbed light is increased, in other words, the number of elementary processes is in-

creased, without altering their character. On the other hand, if there is a spectral shift of the whole band, it would follow that the amount of energy required by the process is altered. If the latter represents the facts, then, as Fig. 27 shows, the adsorbed silver ions cause a shifting toward the region of longer wave lengths which means that the amount of energy required to transfer an electron from a bromine ion to a silver ion has been decreased by the adsorbed silver ions.

Fajans and Karagunis [20] made absorption measurements on silver iodide where the whole absorption band is available for study. The results are shown graphically in Fig. 28. With this salt also was observed an increase in absorption of the silver body in comparison with

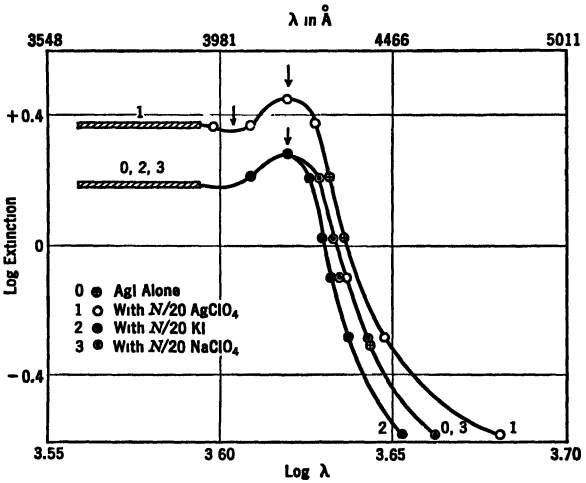


FIG. 28.—Influence of adsorbed ions on the absorption of light by silver iodide.

normal silver iodide and the iodide body. The maximum in the absorption band was scarcely shifted, however, the whole curve of the silver body being raised fairly uniformly in comparison with that of normal silver iodide. These observations indicate that there is no change in the energy requirements but only an increase in the number of absorbing molecules or ions. A silver iodide surface coated with adsorbed silver ions absorbs a larger portion of the incident light than an equal amount of a normal surface; hence more of the former is decomposed. It is probable but not proved that adsorbed silver ion on

[20] Z. physik. Chem., **B5**, 385 (1929); Naturwissenschaften, **17**, 274 (1929).

silver bromide likewise raises rather than shifts the absorption band.

The effects are so pronounced that they are easy to demonstrate.[21] For example, it was found under given experimental conditions that silver bromide in the presence of potassium bromide solution was not noticeably colored except by violet light whereas the same salt in contact with silver nitrate was colored more or less throughout the whole range of the visible spectrum down into the red. A similar behavior was observed with silver chloride.

These observations indicate strongly that light absorption by the silver halides with the concomitant chemical change is influenced markedly by adsorbed silver ions. This raises the question as to how adsorption of ions influences the absorption of light. Fajans interprets the phenomenon as a result of the deformation of ions[22] which can be represented first as a polarization or induced dipole formation and second as a distortion of the electron orbits of the atom. In any event, the change in photochemical sensitivity is associated in some way with disturbance of the space lattice of the surface of the absorbing crystals.[23]

The optical sensitivity of a silver halide increases with the *p*H value, being more pronounced above $p\mathrm{H} = 7.5$. This has been attributed by Fajans to the adsorption of OH^- ions[24] which possess a lower electron affinity than halide ions and to the deforming action of the silver ions of the lattice on the adsorbed ions.

Sensitization by Colloidal Silver. In 1867 Becquerel[25] reported that silver chloride papers after exposure to blue-violet or white light gave an enhanced visible image on further exposure to yellow and red rays. It was demonstrated by Lüppo-Cramer[26] that this is due to direct optical sensitization by colloidal silver. The sensitization of ordinary photographic plates by treating with bisulfite and washing with alkaline water[27] is probably due both to colloidal silver and to

[21] Fajans and Frankenburger: Z. Elektrochem., **28**, 499 (1922); Frankenburger: Z. physik. Chem., **105**, 273 (1923); Steiner: **125**, 275; Fajans and Steiner: 307 (1927).

[22] Fajans: Z. Krist., **61**, 29 (1925); Z Elektrochem., **34**, 506 (1928); Fajans and Karagunis: Z. physik. Chem., **B5**, 385 (1929).

[23] *Cf.* Sheppard and Vanselow: J. Phys. Chem., **33**, 250, 331 (1929); **34**, 2719 (1930); Hevesey: Z. physik. Chem., **101**, 337 (1922); Gudden and Pohl: Z. Physik, **16**, 42 (1923); Pohl: Naturwissenschaften, **14**, 214 (1926).

[24] *Cf.* Rabinovich and Bogdassaryan: Z. wiss. Phot, **32**, 97 (1933).

[25] "La Lumiere," Paris, 176 (1867).

[26] Phot. Korr., **46**, 269, 339, 579 (1909); **47**, 21 (1910).

[27] Capstaff and Bullock: Brit. J. Phot., **67**, 719 (1920).

adsorption of hydroxyl ions, as noted above. Treatment with thiosulfate likewise produces sensitization,[28] probably because of the formation of colloidal silver sulfide.[28]

Fajans attributes the optical sensitization of colloidal silver, like that of adsorbed silver ion, to change in the absorption of light as a result of deformation of silver halide by adsorbed silver. Sheppard,[29] on the other hand, attributes the sensitizing effect primarily to sensitized photoelectric electron emission by silver amicrons and ultramicrons, rather than to ionic deformation.[30]

Sensitization by Dyes. Two principal classes of dyes have been found especially useful as optical sensitizers: (*a*) phthaleins, such as erythrosin and eosin, which are acid dyes; and (*b*) cyanins, such as carbocyanins and isocyanins, which are basic dyes. According to Bancroft [31] an optical sensitizer in photography, in cases in which fluorescence is barred, is a "colored substance which is adsorbed by silver bromide, which does not bleed into gelatin sufficiently to form a color screen, and which is either a powerful enough reducing agent to produce a latent image with silver bromide when activated by light or is converted by light into a reducing agent sufficiently powerful to produce a latent image with light."

The above definition seems to cover the ground practically but it leaves unanswered the mechanism by which the adsorbed dyes effect the sensitization. It has been suggested that the adsorbed dye molecules are excited by the light and transfer their absorbed energy by second-order collisions to silver halide or halide ion similar to the photochemical sensitization of gas reactions by excited mercury atoms.[32] This may be represented by the following scheme, where D stands for dye and D_{Ex}, the excited dye.

$$D + h\nu \rightarrow D_{Ex}$$
$$D_{Ex} + \mathrm{Br}^- \rightarrow D + \mathrm{Br} + \theta$$
$$\mathrm{Ag}^+ + \theta \rightarrow \mathrm{Ag\ (silver\ atom)}$$

If this be true the same molecule of dye could assist in the decomposition of an indefinite number of silver halide molecules. The process

[28] *Cf.* Sheppard, Wightman, and Trivelli: J. Franklin Inst., **204**, 491 (1927).
[29] J. Franklin Inst., **210**, 587 (1936).
[30] *Cf., also,* Eggert and Noddack: Z. Physik, **31**, 922 (1925).
[31] Bancroft, Ackerman, and Gallagher: J. Phys. Chem., **36**, 154 (1932); Colloid Symposium Monograph, **9**, 154 (1931).
[32] *Cf.* Sheppard: J. Franklin Inst., **210**, 587 (1930); Ind. Eng. Chem., **22**, 555 (1930).

cannot be a collisional transfer only, since Leszinski [33] showed that the absorption of light by one molecule of erythrosin gives at least 20 silver atoms of visible decomposition of silver halide. Sheppard and Crouch [34] observed two conditions of adsorption of the basic dye orthochrome T to silver bromide: one, an approach to monomolecular adsorption when the dye is in true solution; and a second, multimolecular adsorption when the solution is so concentrated that the dye is in part in colloidal solution. The maximum effect in optical sensitization was found well below the level of concentration necessary for the formation of a complete monomolecular layer, indicating that the sensitization is effected in monomolecular patches of relatively few dye molecules. If the collision hypothesis were correct it would seem that any strongly adsorbed dye should act as a sensitizer for its own absorption band. But, as already pointed out, many strongly adsorbed dyes do not sensitize at all and only two groups are actually useful technically.

A second hypothesis is that the adsorbed dye gives up electrons on absorption of light in their own absorption band and that these electrons reduce the silver ions, the residual organic radical at the same time undergoing further chemical change. From this point of view the anion of an acid dye adsorbed to a silver ion might easily transfer its valence electron to the silver ion, giving a silver atom; but it is less obvious how the adsorbed cation would lose an electron to silver ion. Yet, so far as is known, the sensitizing behavior of both classes of dyes is quite similar.

Since the sensitizing dyes are usually bleached or oxidized in light and the change is accelerated by silver salts both in solution and as solid adsorbents for the dyes, it is possible that the sensitizing action consists in a photoreduction by the dye. Kögel and Steigmann [35] suggest that the dye in light acts as a reducing agent by way of hydrogen released from water. This like the other theories is without quantitative experimental support.

Photographic Emulsions

The photographic emulsions, so called, are suspensions of the light-sensitive silver halides in a colloidal medium such as collodion or gelatin. Layers of silver bromide prepared by sedimentation of the sols

[33] Z. wiss. Phot., **24**, 261 (1926).
[34] J. Phys. Chem., **32**, 751 (1928).
[35] Z. wiss. Phot., **24**, 18 (1926).

have been used for photographic investigations [36] and for plates sensitive to the ultraviolet; [37] but, for most purposes, the sols formed in the presence of gelatin are employed. Since the properties of silver halide sols vary considerably depending on whether they are formed in the presence of a slight excess of soluble silver salt or in the presence of a slight excess of alkali halide, it has been found practicable to distinguish two classes of silver halide emulsions.

Technical emulsions formed in the presence of excess soluble silver salt, usually silver nitrate, include "wet collodion," which is used extensively in photomechanical work, and collodion emulsions for printing out. Silver ions adsorbed on the halide ions of the silver halide lattice sensitize the primary photochemical decomposition of the salt, and, as already noted, the silver nitrate may also act as a chemical sensitizer by combining with bromine liberated by the primary light process.

The group of emulsions formed in the presence of excess alkali halide comprise both positive and negative emulsions for development. The excess soluble halide influences the physical character of the precipitated salt chiefly by acting as a solvent in the "ripening" process which will be considered in a later paragraph. In the preparation of most negative emulsions, soluble iodide up to 5% of the silver halide is added to the alkali bromide so that the resulting silver bromide contains a small amount of silver iodide. Emulsions used for photographic papers may consist of nearly pure silver bromide, of mixtures of silver bromide and chloride, or, in some instances, of pure silver chloride.

The precipitation of the silver halide must be carried out under carefully controlled conditions in order to prevent flocculation of the particles and to ensure uniform dispersion throughout the gelatin. The action of gelatin as a protecting colloid tends to give a fine-grained uniform precipitate which always consists of crystalline particles. The adsorption of gelatin to the crystals is so strong that a monomolecular layer exists on them even after digestion in boiling water for several hours.[38] In commercial positive emulsions, the particles seldom exceed 0.3μ in diameter; those in negative emulsions, 3 to 4μ. Actually, there is usually a wide variation in grain size. Sheppard and his co-

[36] Herschell: Hunt's "Researches on Light," London, 66 (1859); Schaum: Eder's Jahrbuch Phot., 74 (1904); Weisz: Z. physik. Chem., **54**, 322 (1906).

[37] Schumann: Sitzber. Akad. Wiss. Wien, Abt. IIa, **102**, 994 (1893).

[38] Sheppard, Lambert, and Keenan: J. Phys. Chem., **36**, 174 (1932); Colloid Symposium Monograph, **9**, 174 (1931).

workers [39] have determined the proportion of grains of different size in given emulsions and have thereby established the grain-size frequency, that is, the relative proportion of grains of different sizes in, say, 1000 grains. The statistical curves of most emulsions can be expressed by probability formulas of the exponential or (modified) Gaussian type. The distribution is of particular importance because of the relation between grain size and sensitivity in a given emulsion.

The Latent Image

The action of light on the silver halides gives products that vary widely in color, depending on the nature and physical character of the halide and the time of exposure to the light. These so-called photo-halides [40] have been found to be colloidal dispersions of silver in silver halide (Vol. I, p. 121).

In photography with development, the exposures of the sensitive plate to light are insufficient to cause any microscopically visible change in the silver halide. Yet some change must take place since the application of suitable reducing agents causes the so-called "latent image" to develop. The nature of the latent image has been a subject of controversy for a long time. Owing to the very slight change in silver halide on short exposure, the latent image was thought to be a physical or allotropic modification of silver halide. Namias [41] assumed polymerization; Hurter and Driffield,[42] depolymerization; Bredig,[43] mechanical disintegration; Jones,[44] a labile form; and Bose,[45] mechanical strain. Bancroft [46] points out that all these assumptions, and the further one of von Tugolessow [47] that the latent image is an oxidation product, are untenable since all the phenomena of the latent image can be duplicated by immersing the plate in a solution of a weak reducing agent such as sodium arsenite.[48] It would appear, therefore, that the latent image is some reduction product of silver bromide. At one time

[39] Wightman, Sheppard, and Trivelli: J. Phys Chem., **27**, 1, 141 (1923).
[40] Lea: Am. J Sci., (3) **33**, 349 (1887).
[41] "Chimie photographique," 102, 110 (1910)
[42] Phot. J, **22**, 149 (1898).
[43] Eder's Jahrbuch Phot, **13**, 365 (1899).
[44] "Science and Practice of Photography," **1**, 383 (1904).
[45] Phot. J., **26**, 146 (1902).
[46] Trans. Faraday Soc., **19**, 243 (1923).
[47] Phot. Korr., **40**, 594 (1903).
[48] Bancroft: J. Phys. Chem., **14**, 294; Perley: 689 (1910); Clark: Brit. J. Phot., **69**, 462 (1922).

this was believed to be either a sub-halide [49] or a series of sub-halides of varying composition.[50] These assumptions appear unfounded since no one has been able to prepare any sub-halide derived from the chloride, bromide, or iodide of silver, and it is improbable that any exists.[51]

A second assumption is that the latent image consists of an infinitesimally small quantity of metallic silver which acts as a germ or nucleus [52] facilitating the reduction of the surrounding silver halide. This view has been criticized on the grounds that the latent image shows none of the reactions of metallic silver,[53] does not exhibit the potential of colloidal silver,[54] and does not account for the facts of development and solarization (image reversal).[55] To get around these difficulties, the latent image was assumed to consist of a phase of variable composition with silver chloride the end term, that is, a solid solution probably of silver in silver halide.[56] It is much more probable that the latent image is an early stage of photo-halide formation and is, therefore, a colloidal solution of metallic silver dispersed in silver halide [57] and possibly adsorbed thereby.[55,46] This view seems to account best for all the reactions of the latent image including the effect of oxidizing agents and the acceleration in reduction shown in developability. Thus, the latent image is destroyed, so far as chemical development is concerned, by treating with chromic acid (2% $CrO_3 + 1\%$ H_2SO_4). On the other hand, if the plate is considerably over-exposed, and the silver halide subsequently removed by sodium thiosulfate, it is possible to develop an image by an acid silver developer such as silver nitrate plus ferrous sulfate and acetic acid. Luppo-Cramer [58] attributes this behavior to the formation of colloidal silver inside the grain by prolonged exposure. Under ordinary conditions,

[49] Luther: Z. physik. Chem., **30**, 680 (1899).

[50] Trivelli: Chem. Weekblad, **7**, 321, 350, 381, 404 (1910); **8**, 101 (1911); **9**, 232, 248 (1912).

[51] Baur: Z. physik. Chem, **45**, 613 (1903); Reinders: **77**, 213, 356, 677 (1911).

[52] Wi. Ostwald: "Lehrbuch allgemeinen Chemie," 2nd ed., **2**, 1078 (1893); Abegg: Arch. wiss. Phot., **1**, 268 (1899); Lorenz: Z. Elektrochem., **7**, 277 (1900).

[53] Lüppo-Cramer: Phot. Korr., **38**, 145 (1901).

[54] Sheppard and Mees: Proc. Roy. Soc. (London), **76A**, 217 (1905); **78A**, 461 (1907); Lüppo-Cramer: Kolloid-Z., **2**, 103, 135 (1908).

[55] Bancroft: J. Phys. Chem., **17**, 93 (1913).

[56] Lüppo-Cramer: "Das latente Bild" (1911); Reinders: Z. physik. Chem., **77**, 213 (1911).

[57] Abegg: Arch. wiss. Phot., **1**, 268 (1899); Lorenz: Z. Elektrochem., **7**, 277 (1900).

[58] "Photo. Probleme" (1907).

these exposed particles are protected by silver halide and so cannot initiate reduction with a developer after the surface latent image is removed by an oxidizing agent. On the other hand, if the protecting silver halide is first removed, the nuclei are uncovered and can act as centers for the deposition of silver from a supersaturated solution. Lüppo-Cramer prepared synthetic photo-halides that behave in the same way as the latent image. If the excess silver is not removed from the photo-halides by the use of too strong an oxidizing agent, they are readily developable; but treatment with chromic acid destroys this property. It thus appears that the latent image does show certain of the reactions of metallic silver. There is, of course, no reason why colloidal silver protected by silver halide should show the same electrical potential as silver in mass.

One objection to considering the latent image as a photo-halide is that the latter is highly colored, whereas the former never is, under ordinary conditions. The difference is apparently merely a question of the amount and degree of dispersity of the colloidal silver. If plates are exposed to the action of x-rays before exposure to ordinary light, the x-ray image develops as a pinkish coloration in contrast with the gray-green tone of the untreated halide.[59] Lüppo-Cramer [60] attributes this difference to the higher degree of dispersity of the silver in the grains exposed to x-rays. The effect of the x-rays is to produce a much larger number of nuclei per grain and hence a larger number of smaller particles with the resulting pink tone. This is in line with the observation that the color of silver hydrosols passes from yellow through brown, red, purple, and blue to gray with increasing particle size.

Since it is now generally agreed that the latent image consists of minute traces of metal, the chief question that remains is its origin. One view assumes that it is already present before the light acts, the function of the exposure being to change its physical state.[61] Renwick suggests that the colloidal silver is present originally as a "negative sol" which is coagulated by light to a "neutral gel" that can catalyze the chemical development. Weigert,[61] on the other hand, assumes that the exposure causes micellar deformation or reorientation of pre-existing specks of colloidal silver, with or without a sensitizer, thereby

[59] Lüppo-Cramer: "Die Röntgenographie," 29 (1909).

[60] Phot. Korr., **47**, 337, 527 (1910).

[61] Weigert: Z. physik. Chem., **B3**, 377 (1929); Weigert and Lühr: Z. wiss. Phot., **28**, 312 (1930); Schmidt and Pretschner: **25**, 293 (1928); **27**, 36 (1929); **28**, 30, 35, 111 (1930).

producing a more active nucleus for catalyzing the action of the developer.

The second and more probable theory of latent-image formation assumes that the silver is released by the photochemical decomposition of the silver halide according to the same primary reaction as the measurable decomposition (p. 144). In support of this, it has been demonstrated that the spectral sensitivities of the silver halides are determined by the halide, a fact established by the behavior of mixtures,[62] whereas, on the basis of Weigert's assumption, the sensitivities should be determined by the specific silver adsorption complex without any reference to the halide. In this connection Sheppard [63] showed that desensitizing plates by means of chromic acid or other oxidizing agent does not change the relative spectral sensitivity distribution although greatly reducing its absolute value.

Furthermore, the observations of Toy and Harrison [64] on the photoconductivity effect of silver halide crystals, that is, the change in conductance on illumination, indicate that the primary light action consists in the release of valency electrons from the bromide ions which are changed into bromine atoms that react with other atoms and molecules such as those in the neighboring gelatin. A permanent change thus takes place with the formation of metallic silver as one of the reaction products.

Further reference to the nature of the latent image will be made in the next section.

Photographic Sensitivity

In an earlier section, attention has been given to the optical sensitivity of the silver halides and the methods of varying it. Photographic sensitivity or developable sensitivity (latent image) is a different effect which will be given special consideration.

Sheppard [65] defines the sensitivity of a photographic emulsion by the exposure in candle-meter-seconds (product of intensity of light and time of exposure) necessary to give a certain normal negative with chemical development behind a sensitometer table. Practically, silver bromide emulsions may be prepared which range from the Lipp-

[62] Huse and Meulendyke: Phot. J, **66**, 303 (1926).

[63] Colloid Symposium Monograph, **3**, 76 (1925).

[64] Proc. Roy. Soc. (London), **127A**, 613, 629 (1930); *cf., also,* Toy and Edgerton: Phil. Mag., (6) **48**, 947 (1924).

[65] Colloid Symposium Monograph, **1**, 346 (1923).

mann type (speed 1) to the high-speed type (speed 150,000). A number of conditions are operative in determining the sensitivity:

Ripening

The speed of an emulsion of the Lippmann type may be increased by ripening in the sense of digestion of the emulsion at temperatures up to 80° in the presence of silver bromide solvents such as ammonia or soluble bromide. Since the ripening process consists chiefly in the dissolution and reprecipitation of silver bromide,[65,66] with the consequent coarsening of grain, it has been generally assumed that a coarse grain is more sensitive than a fine one. This is only partly true, since grains of the same size may differ in sensitivity when present in different emulsions. Thus, mere ripening of an emulsion of the Lippmann type might increase the speed five hundredfold or more, but it will not give an emulsion of the high-speed type. Such emulsions are, in general, prepared with relatively high concentrations of the reacting silver salt and alkali bromide, low gelatin concentration, high temperature of mixing, and retarded addition, so that the dispersity of grain is determined at mixing and is altered but little by ripening.[67] The extended investigations of Sheppard and his collaborators on the grain-size distribution in a large number of different emulsions disclose that though coarseness of grain is a necessary condition, it is not a sufficient condition [65] for high speed. In general, the sensitivity increases statistically with the size of grain in one and the same emulsion, but with different emulsions there is no necessary relation between average grain size and sensitivity. The absence of a definite correlation between grain size and sensitivity suggests that some other factor is operating.

The Sensitivity Substance

It is a well-known fact that a much faster plate is obtainable with gelatin than with dry collodion. The formal way to account for this is to assume that gelatin is a better sensitizer than collodion since gelatin will react with bromine more readily than collodion does and hence is a better depolarizer. This cannot be the whole explanation since different gelatins show marked differences in their sensitizing action. For the same reason, it is not permissible to attribute the

[66] Sheppard and Lambert: Colloid Symposium Monograph, **4**, 281 (1926); *cf., however,* Renwick: Phot. J., **64**, 324 (1924).

[67] Trivelli and Sheppard: "The Silver Bromide Grain of Photographic Emulsions," Van Nostrand, 104 (1921).

superiority of gelatin over collodion to the possibility of producing larger individual crystals of silver bromide in the former medium than in the latter.

Some years ago Luppo-Cramer [68] showed that the sensitivity of ripened photographic plates was diminished appreciably by treatment with chromic acid before exposure, followed by thorough washing. Lüppo-Cramer accounted for this behavior by postulating the existence of "Reifungskeime" or sensitive nuclei of highly dispersed colloidal silver.[69] Sheppard [70] and his collaborators showed that practically every kind of photographic emulsion could be desensitized in this way and pointed out the relation between this phenomenon and the destruction of the latent image by chromic acid and other oxidizing agents. It was shown further that the smaller grains were reduced relatively more in sensitivity than the larger ones by the chromic acid treatment.[71] It was evident, therefore, that the silver halide grain contains a sensitivity substance other than silver bromide which increases photographic sensitivity and is destroyed by chromic acid.

A fundamental advance which made possible the isolation and identification of the sensitivity substance was made at the Eastman Kodak Company by R. F. Punnett. He succeeded in obtaining from a gelatin which yielded highly sensitive emulsions an extract which could be added to emulsions of low sensitivity and thereby increase both their speed and density-giving power. A systematic search for this sensitizing material showed it to consist for the most part of certain organic sulfur-containing substances, such as mustard oil and bodies derived therefrom.[63] The action of these may be illustrated by taking allyl mustard oil as an example. This compound reacts with ammonia as follows:

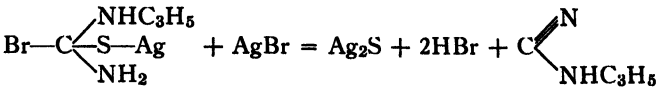
$$C_3H_5CNS + NH_3 = C(=S)(NHC_3H_5)(NH_2)$$

the thiocarbamide formed reacting with silver halide in excess to give a relatively insoluble silver salt:

$$C(=S)(NHC_3H_5)(NH_2) + AgBr = Br{-}C(-S{-}Ag)(NHC_3H_5)(NH_2)$$

[68] "Phot. Mitteilung," **328** (1909).
[69] *Cf., also,* Renwick: J. Soc. Chem. Ind., **39**, 156*T* (1920).
[70] Sheppard, Wightman, and Trivelli: J. Franklin Inst., **196**, 779, 802 (1923).
[71] *Cf., also,* Clark: Phot. J., **63**, 230 (1923).

These compounds do not appear to be the actual sensitizers, for, on treating with slightly alkaline solutions, silver sulfide is formed in some such way as the following:



Since definite sensitization is obtained only after treatment of the emulsion at sufficiently high *p*H value to produce Ag_2S, it is probable that this compound is the effective sensitizer.

The existence in gelatin of varying amounts of sulfur bodies which yield the sensitizer, silver sulfide, accounts for the facts that gelatin emulsions are more sensitive than collodion emulsions and that gelatin emulsions made with different samples of gelatin, but otherwise similar, may exhibit marked differences in sensitivity. The action of chromic acid in cutting down the sensitivity substance is due sometimes, perhaps, to destruction of the mustard oil impurity, but more generally to destruction of silver sulfide nuclei.

Mechanism of the Sensitization. Trivelli and Sheppard [72] first showed that the photochemical decomposition of the octahedral surfaces of silver bromide crystals does not take place simultaneously over the entire surface of the crystal but starts at isolated points. Similarly, Hodgson [73] found that, if the development of exposed single grains was carried out with a dilute developer and interrupted at an early stage before the grain was completely reduced, the development was observed to commence at one or more isolated points on the grain. Svedberg [74] and Toy [75] showed these sensitivity centers to be statistically distributed among the grains in a purely haphazard manner. Further, it appeared to be sufficient for a grain to have one such development center in order to be completely developable while the chance of a grain having one such center at a given exposure to light increased with the size of the grains in one and the same emulsion. As already noted, Sheppard, Wightman, and Trivelli [76] showed that treatment of an emulsion with chromic acid, prior to exposure, desensitizes

[72] "The Silver Bromide Grain of Photographic Emulsions," Van Nostrand, 83 (1921); Phot J., **63**, 334 (1923); J. Phys Chem., **29**, 1568 (1925); *cf., also,* Lorenz and Eitel: Z. anorg. Chem., **91**, 57 (1915).

[73] J. Franklin Inst, **184**, 705 (1917).

[74] Phot. J., **62**, 180, 310 (1922).

[75] Phil. Mag, (6) **44**, 352 (1922); Trans. Faraday Soc., **19**, 290 (1923).

[76] J. Franklin Inst., **196**, 674 (1923).

the smaller grains to a greater extent than the larger ones. The sensitivity spots therefore must exist prior to exposure and are not produced either by exposure [77] or by development. It now appears that these nuclei are silver sulfide particles [78] which exist at certain points in the crystal lattice of the bromide, causing a localized concentration of the photochemical effect whereby the same light energy which would have produced silver atoms dispersed about the silver halide crystal produces the same number immediately contiguous to the silver sulfide, thereby affording a nucleus for development for a correspondingly smaller exposure.

From this point of view the latent image consists of colloidal silver on nuclei of silver sulfide. It has been suggested [79] that the silver sulfide nuclei are surrounded by halos of deformed ions in the silver halide lattice in such a way that light falling on the grain is oriented toward the centers and the photochemical reduction of the halide takes place in their immediate vicinity. It is supposed that a center makes a grain developable when it reaches a certain size and the orienting effect of a center grows with the formation of silver, in other words, is autocatalytic. On this theory, the greater sensitivity of the larger grains in the same emulsion is a consequence both of the increased chance that a larger grain has a larger sulfide nucleus and of the increased mass of silver salt available to afford oriented photoproduct. Disintegration by chromic acid is due primarily to the destruction of the silver sulfide nuclei which are active in initiating the localized decomposition. Any residual sensitivity after chromic acid treatment is probably due to nuclei which are protected by the silver halide.

An interpretation of the photolytic process in the silver halide lattice from the point of view of the quantum mechanics of crystals has been given by Webb.[80]

Action of Silver Iodide

It has been pointed out that silver iodide up to 5% is usually present in silver bromide emulsions; more than 5% is detrimental since it reduces the developability. Now the crystal structure of silver bro-

[77] *Cf*, *however*, Silberstein: Phil. Mag, (6) **44**, 257, 956 (1922).

[78] Sheppard: Phot. J., **49**, 380 (1925).

[79] Sheppard, Trivelli, and Loveland: J. Franklin Inst., **200**, 51 (1925); Trivelli: **204**, 649 (1927); Sheppard and Trivelli: Phot. Korr., **64**, 145, 173, 242, 273 (1928); Sheppard Phot. J., **68**, 397 (1928).

[80] J. Optical Soc. Am., **26**, 367 (1936).

mide is simple cubic of open type, whereas that of silver iodide is tetrahedral of a much more compact form. X-ray analysis [81] shows that the presence of silver iodide in the silver bromide lattice enlarges the lattice and consequently induces changes in the interatomic forces. This produces a condition of strain which renders the mixture more light sensitive than the simple bromide lattice. Fundamentally, the iodide ion is an optical sensitizer—it loses an electron for a lower quantum number. The effect is, perhaps, still further enhanced by the presence of the foreign colloidal particles of silver sulfide within the lattice.

An examination of certain high-speed iodobromide emulsions by Renwick and his collaborators [82] disclosed the presence of more iodide in the larger grains than in the smaller ones. It has been inferred from this that the apparent relation of size of grain to sensitivity in the same emulsion may be caused entirely by the greater proportion of iodide in the larger grains. Sheppard and Trivelli [83] disproved this assumption by showing that the larger grains of a silver bromide emulsion free from iodide are markedly more sensitive on the average than the smaller grains. Steigmann [84] reports that the addition of colloidal silver iodide to emulsions exerts a restraining action on the ripening of the emulsion both in regard to the size of grain and to the sensitizing action of the gelatin.

Development

The development of the exposed photographic plate consists essentially in the conversion of silver ions to metallic silver. Technically, two types of development are distinguished: (1) "Physical" development, so called, in which the silver which builds up the developed image on the colloidal silver nuclei of the latent image is obtained from soluble silver salt in the developing solution. Owing to the high concentration of silver ions, the reduction potential is low and reducers are employed in acid solution. (2) "Chemical" development, in which silver is formed by reduction of the solid silver halide grains themselves, the reduction being catalyzed by the silver nuclei of the latent

[81] Wilsey: J. Franklin Inst., **200**, 739 (1923); Slater-Price: Phot J., **75**, 447 (1935).

[82] Renwick and Sease: Colloid Symposium Monograph, **2**, 37 (1925); Phot. J., **64**, 360 (1924); Baldsiefen, Sease, and Renwick: **66**, 163 (1926); *cf* Luppo-Cramer: Z wiss. Phot., **27**, 9 (1929).

[83] J. Franklin Inst., **203**, 829 (1927).

[84] Phot. Ind., **27**, 375 (1929).

image. In this case, higher reduction potentials are employed, the solutions being alkaline.[85]

The commonly held theory of the development of the latent image is that the developer is a reducing agent sufficiently powerful to reduce exposed silver bromide which has a nucleus in each grain on which the deposition of silver can take place, but not powerful enough to reduce unexposed silver bromide.[86] Bancroft [55] points out that this theory is in itself inadequate since measurements of the electromotive force of developers and of silver bromide before and after exposure fail to substantiate the theory.

In general [46] a photographic developer must be a fairly strong reducing agent, but such substances as stannous chloride, *m*-aminophenol, formaldehyde, and gallic acid do not give a satisfactory negative. All developers will develop gelatin-free silver bromide readily, irrespective of whether the silver salt has been exposed to light. Most developers will give negatives after very short exposures and positives after very long ones; but some give positives even with very short exposures. With a given developer, the exposure necessary to cause a change from negative to positive varies with varying concentration of the developer. Some developers work rapidly and others slowly, the difference not always being a question of reducing power, although this is important.

Since a negative may result with one developer and a positive with another, it is apparent that the potentials of exposed and unexposed silver bromide are not the only factors. If this were true, a negative would always be obtained with one exposure and a positive with another, irrespective of the developer. The developer must therefore have functions other than those of reducing agents with different strengths. To account for the varying behavior, Bancroft postulates that the developers are selectively adsorbed at the surface of the grain giving markedly varying concentrations at these surfaces. If the developer is adsorbed much more strongly by exposed silver bromide than by the unexposed halide, the former will develop more rapidly, giving a negative; if the conditions are reversed, a positive will result; and if there is little difference in the adsorptions, the development will be more or less uniform over the whole plate. As Bancroft points out, the adsorption theory enables one to predict the three types of fairly

[85] *Cf.* Sheppard and Mees: "Theory of the Photographic Process"; Nietz: "The Theory of Development," Van Nostrand (1922).

[86] *Cf., for example,* Nietz: Phot. J., **60**, 281 (1920).

strong reducing agents actually encountered, but it does not necessarily mean that the developers behave in this way.

Sheppard and Meyer [87] are likewise of the opinion that adsorption of the reducer to the silver halide grain is the first phase of development. They suggest that the free silver ions of the crystal lattice hold ions of the reducer by electroaffinity, the adsorption complex thus formed breaking down in the presence of the nuclei of colloidal silver. Selective adsorption doubtless plays an important rôle also in the effects of certain dyestuffs, some of which accelerate development and others of which desensitize the halides to such an extent that development can be carried out in strong yellow or even white light.[88]

Bancroft believes that the selective adsorption which he postulates involves more or less peptization and that there exists a transition from weakly peptizing, strongly reducing to strongly peptizing, weakly reducing developers, the furthest examples of the latter giving direct solarized or reversed images. In support of his view, Bancroft [46] succeeded in destroying the developability of an exposed plate by washing with elon (metol) containing no alkali, so as to exclude reduction. This was also observed by Luppo-Cramer and confirmed by Sheppard,[89] who, however, questions whether this is truly a peptization of the latent image and suggests that it may be due to slight etching of the surface layers of the silver halide by the reducers which form soluble complexes with silver halides. In the same connection, Sheppard points out that the production of direct positives by development is associated with the formation of "dichroic fogs," colored forms of colloidal silver produced when a solvent for silver halide is present in the developing solution.

A modification of the adsorption theory of development has been put forward by Rabinovich.[90] According to this, the silver nuclei of the latent image themselves selectively adsorb the developing agent. Mention should also be made of the work of Reinders [91] and of Beukers [92] which has brought forward new quantitative evidence for the importance of the oxidation-reduction potential in photographic development.

[87] J. Am. Chem. Soc., **42**, 690 (1920).

[88] Lüppo-Cramer: "Negativentwicklung bei hellem lichte (Safraninverfahren)," Liesegang's Verlag., M. Eger, Leipzig (1921).

[89] Bogue's "Theory and Applcation of Colloidal Behavior," **2**, 776 (1924).

[90] Z. wiss. Phot., **33**, 57; Peisakhovich: 94 (1934).

[91] J. Phys. Chem., **38**, 783 (1934).

[92] "Fotografisch Outwikkerlaars," Thesis, Delft (1936).

PART III

THE COLLOIDAL SULFIDES

CHAPTER IX

COLLOIDAL ARSENIC TRISULFIDE: GENERAL PROPERTIES

The Precipitated Salt

Physical Character

Arsenic trisulfide is thrown down as a citron-yellow flocculent mass or gel by passing hydrogen sulfide into a solution of arsenic trioxide acidified with hydrochloric acid. Spring[1] claimed to get a definite hydrate, $As_2S_3 \cdot 6H_2O$, by drying the gel at 20° in air having a relative humidity of 70%. The specified volume of the alleged hydrate was greater than that of the sum of its constituents; hence water was removed by applying 6000–7000 atmospheres pressure. In spite of the analysis and the behavior under pressure, it is unlikely that Spring's preparation was other than arsenic trisulfide with adsorbed water, the composition of which like that of any hydrous precipitate could be varied continuously by changing the conditions of drying.

Evidence of the colloidal character of the precipitated sulfide is furnished by the observation that the freshly formed gel is decomposed appreciably by water, giving hydrogen sulfide and arsenious acid, whereas the gel previously heated to 125° is more stable.[2] When carried out carefully, the estimation of arsenic as arsenic trisulfide can be done with quantitative accuracy,[3] but Schmidt[4] claims that the precipitate contains traces of $As(SH)_3$ and As_2O_3, the respective errors produced thereby being in opposite directions and so equalizing each other.

Films of arsenic trisulfide formed by the action of hydrogen sulfide on the surface of arsenic trichloride solutions are said to be hydrophilic and to have a layer structure 180–200 molecules thick.[5]

[1] Z. anorg. Chem., **10**, 185 (1895).

[2] Clermont and Frommel: Compt. rend, **87**, 330 (1878); Chodounsky: Chem. Zentr., I, 569 (1889); *cf.* Cross and Higgin: Ber., **16**, 1195 (1883).

[3] Puller: J. Chem. Soc., **24**, 586 (1871); Friedheim and Michaelis: Z. anal. Chem., **34**, 505 (1895).

[4] Arch. Pharm., **255**, 45 (1917); Chem. Abstracts, **11**, 3005 (1917).

[5] Demenev and Mokruschin: J. Phys. Chem. (U. S. S. R.), **7**, 763 (1936).

Color. The citron-yellow precipitate thrown down with hydrogen sulfide from acid solution dries to an impalpable yellow powder. In addition to the yellow product Winter [6] prepared what he called a red allotropic modification of the trisulfide by freezing or evaporating the hydrosol, or by coagulating the hydrosol by a salt or acid followed by drying. The observations and conclusions of Winter were opened to question by more recent work of Semler [7] and of Bhatnagar and Rao.[8] Semler was unable to prepare a red sulfide except by coagulating the arsenic trisulfide sol with an electrolyte which was believed to give a red sulfarsenite; thus a red preparation was obtained by coagulating the sol with barium chloride but not with sodium chloride. Bhatnagar and Rao claimed that the red preparation was not the trisulfide As_2S_3 but more nearly the disulfide As_2S_2.[9]

Winter's view that the yellow and red sulfides are allotropic modifications resulted from the observation that the red preparation changed to yellow on standing for a long time at room temperature or by prolonged heating at 150–160°. He could not establish the existence of an inversion point, however, and the color change is exactly the reverse of that observed by Borodowski,[10] who reported that the yellow form was stable up to a temperature of 170° where it changed to red.

Semler's conclusion, that the red color obtained by coagulating arsenic trisulfide sol with barium chloride results from the formation of red $Ba_2As_2S_5$, lacks experimental justification. In the first place, there is no direct evidence of the formation of this compound on adding barium chloride to a purified arsenic trisulfide sol; and in the next place, the color of barium sulfarsenite is apparently not such as to mask the yellow color of the sulfide with red. Berzelius [11] describes the sulfarsenite of barium as a gummy reddish-brown mass which dissolves completely in water, giving a colorless solution. Nilson,[12] on the other hand, characterizes the pyrosulfarsenite, $Ba_2As_2S_5 \cdot H_2O$, as grayish green in color, changing to indigo-blue when allowed to remain in contact with the mother liquor for some time. The blue color is probably due to colloidal sulfur dispersed in the salt.[13] The orthosulfarsenite is described as slightly soluble pale yellow prisms which

[6] Z. anorg Chem., **43**, 228 (1905).
[7] Kolloid-Z., **34**, 209 (1924).
[8] Kolloid-Z., **33**, 159 (1923).
[9] *Cf.* Bhatnagar: J. Phys. Chem., **35**, 1803 (1931).
[10] Chem. Zentr., II, 297 (1906).
[11] Pogg. Ann., **7**, 142 (1826).
[12] J. prakt. Chem., (2) **12**, 295 (1875); **14**, 145 (1876); **16**, 93 (1877).
[13] *Cf.* Mellor: "Inorganic and Theoretical Chemistry," **9**, 296 (1929).

would have little effect on the yellow color of arsenic trisulfide. Finally, if one admits that barium sulfarsenite is formed on adding barium chloride to arsenic trisulfide sol and that the color of the sulfarsenite is red, there is no justification for assuming that sufficient amount will be retained by the sulfide to impart a distinct red color to it. It has been demonstrated that but 0.1 milliequivalent of barium is adsorbed per gram of arsenic trisulfide during coagulation of the trisulfide sol (p. 203). The adsorbed barium is probably associated chiefly with HS^- and S^{--} ion on the sulfide and not with sulfarsenite anion. Even if one makes the improbable assumption that all the barium is present as $Ba_2As_2S_5$, there would be but 1 mol of sulfarsenite to 160 mols of trisulfide.

Bhatnagar and Rao's contention that the red sulfide is not As_2S_3 but As_2S_2, or colored by As_2S_2, is based largely on the results of an analysis of a red product formed by coagulating an As_2S_3 sol, freed from hydrogen sulfide and kept in the dark. It is claimed that As_2S_2 is formed in accord with the following equation: $As_2S_3 + H_2O \rightarrow As_2S_2 \cdot H_2S + O$.

Bikerman [14] obtained a red precipitate by prolonged boiling of a yellow arsenic trisulfide organosol in nitrobenzene. Merely heating the sol above 100° changed it to red, the yellow color returning at a lower temperature with no definite point of transformation. It is obvious that, in a non-aqueous medium, As_2S_2 could not be formed in accord with the scheme of Bhatnagar and Rao nor could a red thioarsenite form in the absence of both metal and hydrogen ion.

An investigation by Weiser [15] of the cause of the variation in color indicates that it is due neither to allotropy nor to differences in composition. In Table XVI are summarized some observations on the color of precipitates that were filtered, washed, and dried in a vacuum desiccator over sulfuric acid. In part (*a*) of the table, the precipitates, 0.435 g, were obtained by conducting hydrogen sulfide into 50 cc of solutions of As_2O_3 containing various electrolytes; and in part (*b*) the same amounts of precipitates were thrown down from a hydrosol with various electrolytes. From these and similar observations, starting with solutions of Na_2HAsO_4, it was found that the color of arsenic trisulfide varies continuously from yellow through orange-yellow, orange, red-orange to red, depending on the conditions of precipitation. The lighter shades always result by direct precipitation, and the darker shades by coagulation of the sol. There is little if any difference in

[14] Z. physik. Chem., **115**, 261 (1925).
[15] Weiser: J. Phys. Chem., **34**, 1021 (1930).

the color of the sulfide precipitated directly in the presence of barium chloride and that thrown down in the presence of potassium or ammonium chloride. The sulfide precipitated in the presence of hydrochloric acid is the familiar yellow irrespective of whether barium chloride is present or absent. The orange-red precipitate formed by coagulation of the sol is the same shade irrespective of the nature of the electrolyte, indicating that the color is not caused by a colored sulfarsenite such as Semler assumed.

TABLE XVI

COLOR OF ARSENIC TRISULFIDES

(*a*) Precipitated directly with H_2S Total volume 50 cc			(*b*) Precipitated from sol Total volume 50 cc		
As_2O_3 14 g/l cc	*N*/2 electrolyte	Color	As_2S_3 sol 10 9 g/l cc	*N*/2 electrolyte	Color
25	LiCl, 10 cc	Orange-yellow	40	LiCl, 10 cc	Orange-red
25	NaCl, 10 cc	Orange-yellow	40	NaCl, 10 cc	Orange-red
25	KCl, 10 cc	Orange-yellow	40	KCl, 10 cc	Orange-red
25	NH_4Cl, 10 cc	Orange-yellow	40	NH_4Cl, 10 cc	Orange-red
25	$BaCl_2$, 10 cc	Orange-yellow	40	$BaCl_2$, 10 cc	Orange-red
25	HCl, 10 cc	Yellow	40	$CaCl_2$, 10 cc	Orange-red
25	HCl, 5 cc + $BaCl_2$, 10 cc	Yellow	40	HCl, 10 cc	Orange-red (slightly darker)

The flocculent precipitate obtained by direct precipitation dries to a yellow powder whereas the more gelatinous mass thrown down from the sol dries to a red horny mass or glass. Both give x-ray diffraction patterns consisting of three bands in the same position as the sharpest lines in the diffraction pattern for orpiment, As_2S_3; both analyze for As_2S_3, and there is no indication of the existence of any appreciable amount of As_2S_2 in the sulfide as ordinarily obtained or in the preparation made according to Bhatnagar and Rao's directions.

The marked differences in the physical character of the yellow and red preparations are probably the underlying cause of the variations in color. These differences are readily accounted for: When hydrogen sulfide is conducted into the hydrochloric acid solution of arsenious oxide, the trisulfide is thrown down in the form of minute amorphous particles, discrete or collected together into loose clumps which disin-

tegrate on drying, giving an impalpable powder. On the other hand, when the gas is conducted into an arsenious oxide solution free from foreign electrolytes, the sulfide appears in the sol state as hydrous ultramicroscopic particles. As has been emphasized repeatedly,[16] the rapid coagulation of hydrous sols favors the formation of a gelatinous precipitate or jelly in which the particles become stuck together or oriented into aggregates forming an enmeshing network which entrains liquid. This is what happens when hydrochloric acid or other electrolyte is added to arsenic trisulfide sol in excess of the precipitation concentration. The gelatinous clumps formed in this way do not disintegrate into a powder on drying, but the minute particles coalesce into a glassy mass that appears orange-red rather than yellow. The color of a transparent chip of the dry sulfide formed from the sol is similar to the color of a thick layer of the relatively concentrated sol viewed by transmitted light.

If the arsenic trisulfide is yellow when in the form of an impalpable powder and red in the form of a horny glassy mass resulting from coalescence of ultramicrons, it would follow that sufficient grinding of the red mass should yield a yellow powder. This was confirmed experimentally. Similarly, the red sulfide was rendered yellow by disintegrating the glassy mass below the sintering temperature. Heating the yellow sulfide in the neighborhood of 175° causes it to sinter, contract, and assume a permanent orange to brown color, depending on the temperature and the duration of the heating.

The red sulfide is stable in the dark and is not affected by light when thoroughly dry. The combined action of light and moisture causes a superficial chemical disintegration of the red sulfide, coating it with a yellow film of sulfide and sulfur.

Arsenic Trisulfide Sol

Preparation

Hydrosols. More than a century ago Berzelius[17] called attention to the formation of a yellow solution when hydrogen sulfide is passed into a pure aqueous solution of arsenious acid. Since arsenic trisulfide precipitated out slowly, Berzelius suggested that the apparent solution was probably a suspension of transparent particles. The colloidal

[16] Weiser: J. Phys. Chem., **26**, 402 (1922); Weiser and Bloxsom: **28**, 26 (1924); (Vol. II, p. 15).

[17] "Lehrbuch der Chemie," 3rd ed., **3**, 65 (1834); *cf.* Graham-Otto: "Lehrbuch der Chemie," **2**, 863 (1840).

nature of the yellow liquid was first definitely recognized by Schulze,[18] who prepared stable sols of widely varying concentrations by passing hydrogen sulfide into arsenious acid solution and removing the excess hydrogen sulfide by boiling or by washing with hydrogen. The limiting concentration of sol obtained in this way is not determined by the solubility of arsenic trioxide in water. Thus Schulze prepared a sol containing 37.5% As_2S_3 by adding small amounts of arsenic trioxide intermittently to a sol into which hydrogen sulfide was bubbled continuously; and Boutaric and Vuillaume [19] obtained one containing 300 g As_2S_3/l by a similar procedure. Picton [20] prepared a sol containing 5 g As_2S_3/l by dissolving arsenic trioxide in a solution of potassium acid tartrate or of sodium hydroxide before adding hydrogen sulfide and then purifying by dialysis.

As would be expected, the sols prepared under different conditions contain particles of widely varying sizes.[21] In a quantitative study of the effect of conditions of sol formation on particle size, Boutaric and Vuillaume [22] found the particles to be larger the greater the concentration of arsenic trioxide, the higher the temperature, the slower the current of hydrogen sulfide, and the larger the excess of hydrogen sulfide. Most modifications of Schulze's procedure have been made with the end in view of obtaining stable sols containing particles of uniform size. Better results are obtained by allowing a dilute solution of arsenic trioxide to drop at a slow uniform rate into hydrogen sulfide water through which the gas is bubbled continuously.[23] The most satisfactory procedure for preparing dilute sols has been worked out by Freundlich and Nathansohn: [24] 50 to 100 cc of cold saturated As_2O_3 solution are diluted to 200 cc and mixed with 100 cc of a solution containing 1 cc of saturated H_2S solution. After a light-yellow coloration appears, the mixture is diluted to 1 l with a hydrogen sulfide solution ten times as strong as the above. Finally, the solution is saturated with the gas, the excess being washed out with hydrogen. The sol gives a faint light cone in the ultramicroscope, but there are no ultra-

[18] J prakt. Chem., (2) **25**, 431 (1882).

[19] J. chim. phys., **21**, 247 (1924); Boutaric and Simonet: Bull. acad. roy. méd Belg., (5) **10**, 150 (1924).

[20] J Chem. Soc., **61**, 137 (1892).

[21] Picton: J. Chem Soc., **61**, 140 (1892); Linder and Picton: **67**, 63 (1895); Biltz: Nachr. kgl Ges. Wiss. Göttingen, **2**, 1 (1906).

[22] Compt. rend., **178**, 938 (1924).

[23] Linder and Picton: J. Chem. Soc., **67**, 63 (1895); Kruyt and van der Spek: Kolloid-Z., **25**, 1 (1919).

[24] Freundlich and Nathansohn: Kolloid-Z., **28**, 258 (1921).

microns. The success of this method of preparation probably lies in the fact that high concentrations of the reacting solutions are avoided and the saturation with hydrogen sulfide is delayed until a large number of arsenic trisulfide nuclei are present.

Concentrated sols which are relatively monodisperse are best prepared by concentrating dilute monodisperse sols by Pauli's process of electrodecantation (p. 115). Thus Pauli and Laub[25] conducted hydrogen sulfide into 18 l of dilute As_2O_3 consisting of 15 l of 50 times diluted, plus 3 l of 15 times diluted, saturated As_2O_3 solution; and concentrated the resulting dilute sol by electrodecantation to a strength of 43.2 g As_2S_3/l. In spite of the relatively high concentration, the resulting sol was pure, perfectly clear, and of a beautiful orange-red color.

On account of the very low solubility of arsenic trisulfide (2.1×10^{-6} mol/l),[26] the transformation to the sol state is quantitative in the presence of a slight excess of hydrogen sulfide.[27] Since the salt hydrolyzes to a certain extent, washing the sol with hydrogen for too long a time results in some decomposition, hydrogen sulfide being carried off and a corresponding amount of arsenious acid remaining in solution.[28]

On mixing 5 cc of 0.1 *N* H_3AsO_3 with 5 to 10 cc of 0.01 *N* H_2S in 300 cc of pure water, there results a clear solution which turns yellow suddenly after a few seconds. If diluted still more, the solution will remain colorless in the dark for several days, although a trace of dilute acids causes it to turn yellow immediately. Since the removal of hydrogen sulfide from the colorless solution with a stream of hydrogen takes place very slowly, Vorländer and Häberle[29] conclude that hydrogen sulfide and arsenic trioxide react in very dilute solution forming an instable molecular compound which is hydrolyzed to a certain extent into the original substances. Semler[30] suggests that this compound may be thioarsenious acid. Peskov[31] makes the more probable assumption that the colorless solution contains ordinary arsenic trisulfide, the absence of color being due to two factors: the ex-

[25] Pauli and Laub: Kolloid-Z., **78**, 295 (1937).

[26] Weigel: Z. physik. Chem, **58**, 293 (1907).

[27] Küster and Dahmer: Z. anorg. Chem., **33**, 105 (1902); **34**, 410 (1903).

[28] Ghosh and Dhar: Kolloid-Z., **36**, 129 (1925); Krestinskaja and Jakowlewa: **65**, 187 (1933).

[29] Ber., **46**, 1612 (1913).

[30] Kolloid-Z, **34**, 213 (1924).

[31] J. Russ. Phys.-Chem. Soc., **46**, 1619 (1914); J. Chem. Soc., **108** (2), 429 (1915).

tremely small magnitude of the primary particles, and, more especially, the complete individuality of the particles. Agglomeration of the fine particles into larger secondary aggregates which appear yellow is prevented in the colorless solution owing to the protecting effect of a relatively large excess of arsenious acid.

Organosols. Bikerman [14] prepared sols of arsenic trisulfide in nitrobenzene and in acetoacetic ester by dissolving dry $AsCl_3$ in the purified and dried solvents and passing dry hydrogen sulfide through the respective solutions. Attempts to make sols in acetone and aniline by the same procedure were not successful. A sol in aniline was obtained by adding realgar (As_2S_2) and sulfur in the right proportions to aniline followed by heating the mixture above the melting point of sulfur.

Ostwald and Wannow [32] obtained sols of arsenic trisulfide in acetic acid, acetic anhydride, and chloroacetic acid as well as in highly concentrated sulfuric acid and phosphoric acid by dissolving arsenic trioxide in the respective solvents and conducting in hydrogen sulfide. Since such sols appear to be uncharged the stability results from strong adsorption of the dispersing medium (p. 242).

Composition and Constitution

Linder and Picton [33] recognized the necessity for a slight excess of hydrogen sulfide for the stability of an arsenic trisulfide hydrosol and therefore concluded that the colloidal sulfides are polymerized hydrosulfides such as $16As_2S_3 \cdot H_2S$. Duclaux [34] proposed the general formula ($n As_2S_3 \cdot x H_2S$) as a basis for explaining coagulation by electrolytes as a purely chemical process. It is common practice to wash out the excess hydrogen sulfide with hydrogen. As we have seen, removal of too much of the gas, either by washing or by oxidation, results in hydrolysis of the sulfide with the formation of arsenious acid more or less of which is adsorbed by the colloidal particles. Accordingly, if the washing has not been carried far enough, the precipitate from the sol will be high in sulfur, whereas if the washing is carried too far or if the sol is aged, especially in the light (p. 176), it will contain excess arsenic as As_2O_3, H_3AsO_3, or H_3AsO_4.[15,35] Pauli

[32] Kolloid-Z., **76**, 159 (1936); *cf.* Voet: J. Phys. Chem., **40**, 307 (1936).

[33] J. Chem. Soc., **61**, 114 (1892).

[34] "Les Colloides," Paris (1920).

[35] *Cf.* Murphy and Mathews: J. Am. Chem. Soc., **45**, 16 (1923); Gazzi: Zymologica, **2**, 1, 10 (1927); Krestinskaja and Jakowlewa: Kolloid-Z., **65**, 187 (1933).

and Semler [36] consider $H_2As_2S_4$ to be the stabilizing electrolyte and the sol to be a strongly dissociated complex acid to which they assigned the formula $(xAs_2S_3 \cdot As_2S_4H_2 \cdot As_2S_4H)^- + H^+$. This formula was made to fit the specific case where but one of four hydrogens is displaced on coagulating the sol with barium chloride, the remaining three appearing in the supernatant solution after coagulation. Considering the sols as strongly dissociated complex electrolytes, attempts have been made to apply the limit laws of Debye-Huckel,[37] but they hold, if at all, only over a narrow concentration range.[38] As a matter of fact, it is now quite generally recognized that the composition of the sol varies with the method of preparation, the excess of peptizing electrolyte, the age, and the treatment to which it is subjected. There appears no good reason for attempting to assign a formula to a mixture of such variable composition. Formed in the presence of hydrogen sulfide the particles adsorb H_2S, and they also adsorb S^{--} and HS^- ions which form the inner portion of the double layer with H^+ ions constituting the diffuse outer portion. The constitution may be represented diagrammatically as shown in part *A* of Fig. 37, p. 212. The particles of an aged sol also contain more or less arsenious acid;[25] and the presence of thioarsenite in small amounts is neither excluded nor established. Kargin and Klimovitzkaja [39] believe that arsenious acid is the stabilizing electrolyte in the sol rather than hydrogen sulfide or thioarsenious acid; but this is improbable especially with hydrogen sulfide in excess.

General Properties

Color. The color of arsenic trisulfide sol varies from red-orange to citron-yellow, depending on the size of the secondary particles and the concentration. A sol with very small particles appears more orange than one of the same concentration containing large particles. A concentrated sol always appears yellower than a dilute one, probably because it is likely to contain larger aggregates. If aggregation is prevented by following the procedure of Pauli and Laub (p. 173), even a concentrated sol possesses an orange color. Because of the marked

[36] Kolloid-Z., **34**, 145 (1924); *cf., also*, Pauli and Laub: **78**, 295 (1937).

[37] Physik. Z, **24**, 185, 305 (1923); Debye: Trans. Faraday Soc., **23**, 334 (1927).

[38] Audubert: Compt. rend, **195**, 210, 306 (1932); *cf.* Hartley: Trans. Faraday Soc., **31**, 31 (1935).

[39] J. Phys. Chem. (U.S.S.R), **5**, 969 (1934).

opalescence and coloring power of the colloidal particles, 1 part of As_2S_3 in 100,000 parts of water can be detected in thin layers.

Boutaric and Vuillaume [40] studied the absorption spectrum of a sol by means of the Fèry spectrophotometer. Designating the intensity of the incident radiation λ by I_0 and the intensity of the radiation after traversing the absorbing medium by I, then, if the sol behaves as a turbid medium, $\log I_0/I$ should vary inversely as the fourth power of λ in accord with Rayleigh's law, where the suspended particles are small compared with λ; and $\log I_0/I$ should vary inversely as some power n of λ for larger particles, n being less than 4 and correspondingly less as the particles are larger. The absorption curve of a sol containing 6.2 g As_2S_3/l did not follow either of these laws but showed a regular increase in n from $n = 33$ for $\lambda = 6400$ to $n = 12$ for $\lambda = 5300$ with $n = 4$ at about $\lambda = 6200$. The absorption thus appears to be the resultant of two phenomena: an absorption by diffusion obeying Rayleigh's law, and a selective absorption caused by the reflection of incident rays from the surface of the particles. The latter absorption should vary with the extent of total surface, diminishing for a constant weight of the sulfide as the size of the particles is increased. In accord with this view, it was found that prolonged boiling, which increases the particle size, decreases the selective absorption. Boutaric [41] showed further that the proportion of polarization of diffused light from the sol decreased with increasing particle size and increased with dilution of the sol.

Action of Light. Although an arsenic trisulfide sol is quite stable when first prepared, the stability decreases on standing, especially in the light. Thus Freundlich [42] observed a decrease in concentration of approximately 15% when a sol was allowed to stand for a year in a closed vessel. Dumanskii [43] placed a sol containing 65 g/l in a vessel 1 m long and 2 cm in diameter, and observed the rate of fall of the particles. The velocity was approximately 0.031 cm per day over a period of 4 years. Since care was not taken to exclude light during the period of observation, it is probable that the settling was due indirectly to the agglomerating effect of light which resulted in the formation of particles sufficiently large to overbalance the effect of Brownian movement.

[40] Compt. rend, **177**, 259 (1923); *cf.* Menon: Kolloid-Z., **76**, 9 (1936).

[41] Boutaric and Tourneur: Compt. rend., **193**, 1011 (1931); *cf* Lange: Z physik. Chem., **132**, 1 (1928).

[42] Z. physik. Chem., **44**, 129 (1903).

[43] Kolloid-Z., **36**, 98 (1925).

The destabilizing action of light on arsenic trisulfide sol was first observed by Young and Pingree.[44] Freundlich and Nathansohn[24] attribute this to the photochemical oxidation of the hydrolysis product —hydrogen sulfide—to colloidal sulfur and pentathionic acid, accompanied by a reaction between the hydrogen sulfide and pentathionic acid which serve as the stabilizing electrolytes for arsenic trisulfide and sulfur, respectively.[45] Removal of the stabilizing electrolytes in this way produces a decrease in the charge on the particles and the consequent precipitation. The electrical conductivity increases to a constant value on exposure to light, the rate of change increasing somewhat with diminishing concentration of sol. Murphy and Mathews[46] attribute this to the building up of a concentration of the thionic acid sufficient to serve as the stabilizing electrolyte for the colloidal sulfur, the reaction between hydrogen sulfide and thionic acid then proceeding at such a slow rate that equilibrium between the several components of the system is maintained and further change in the conductance is prevented. The rate of change of conductivity increases somewhat with diminishing concentration of electrolyte, probably owing to the increased photochemical activity of the sol per unit mass of arsenic trisulfide brought about by the greater dispersity of the more dilute sol. Pauli and Laub[25] believe that the sulfur comes from the photochemical decomposition of sulfo complexes which they assume to exist in the sol.

The appearance of a sol changes on exposure to light not only because of agglomeration of particles but also because it is transformed into a complex mixture.[47]

Density and Viscosity. The density of arsenic trisulfide sols varies linearly with the concentration[48] up to about 9%, above which it increases more rapidly.[49] For concentrations up to 3.6% the index of refraction is also a linear function of the concentration. The refractive index is apparently independent of the degree of dispersion.[50]

The density of the colloidal particles of arsenic trisulfide has been

[44] J. Phys Chem., **17**, 657 (1913); *cf., also,* Boutaric and Manière Bull. acad. roy. méd. Belg., (5) **10**, 571 (1924)

[45] Freundlich and Scholz: Kolloid-Beihefte, **16**, 234 (1922).

[46] J. Am. Chem. Soc., **45**, 16 (1923).

[47] *Cf* Weiser: J. Phys. Chem., **34**, 1021 (1930); Krestinskaja and Jakowlewa: Kolloid-Z, **65**, 187 (1933); Joshi, Barve, and Desai· Current Sci, **3**, 105 (1934).

[48] Linder and Picton: J. Chem. Soc, **67**, 71 (1895); Wintgen: Kolloid-Beihefte, **7**, 266 (1915).

[49] Boutaric and Simonet: Bull. acad. roy. méd. Belg, (5) **10**, 150 (1924).

[50] Lifschitz and Beck: Kolloid-Z., **26**, 10 (1920).

estimated by Dumanskii [51] by applying Einstein's [52] formula for the viscosity of suspensions of rigid spheres,

$$\eta = \eta_0(1 + kf) \tag{1}$$

where η is the viscosity of the sol, η_0 the viscosity of the pure liquid, f the volume of the suspended particles, and k a constant which Einstein at first took to be unity but which he later made 2.5. From viscosity measurements, f can be determined, and, if the concentration of the suspended particles c is known, d the density of the particles follows from the expression

$$d = \frac{c}{f} \tag{2}$$

Since the particles adsorb water, the value of c cannot be determined analytically. This is obtained indirectly from the density of the sol d_s, the density of the medium d_w, and f. Thus

$$d_s = d_w + c - \frac{c}{d}d_w \tag{3}$$

but since

$$\frac{c}{d} = f \tag{2}$$

$$c = d_s - d_w + fd_w$$

Taking the value of k in Einstein's equation as unity, Dumanskii finds the density of the particles of colloidal As_2S_3 to be 1.50 ± 0.02. Later he makes $k = 2.5$ and so concludes that f, from Equation (2), is 2.5 times larger than it should be, and so calculates d to be 3.75 ± 0.12. Dumanskii seems to have completely overlooked the fact that, if f is 2.5 times larger than it should be in his original equation, this will change the calculated value of c also. Had he calculated d from Equatons (1) [$k = 2.5$], (2), and (3), as he says he did, the value of d would come out to be 1.90. This value would appear to be much nearer correct than 3.75, since the particles with their adsorbed water must be less dense than the crystalline mass of As_2S_3 whose density is 3.45. There is, however, no reason to believe that density determinations involving the use of Einstein's equation are any more than first approximations, at best. As already mentioned, Einstein first made

[51] Kolloid-Z., **9**, 262 (1911); **12**, 6; **13**, 222 (1913).

[52] Ann. Physik, (4) **19**, 289 (1906); **34**, 591 (1911); Kolloid-Z., **27**, 137 (1920).

$k = 1$ and later changed it to 2.5; Bancelin [58] found k to be 2.9 for a suspension of gamboge, and Hatschek [54] used $k = 4.5$. According to these formulas, the viscosity is independent of the degree of dispersion, which is not the case. Thus Odén [55] found the viscosity of sulfur sols in which the particles have a diameter of 10 $m\mu$ to be 50% greater than with sols in which the sulfur particles have a diameter of 100 $m\mu$ (Vol. I, p. 336). Hatschek [56] attributes this to the presence of an adsorbed layer of water on the particles which increases the effective volume of the smaller particles much more than the larger ones. Boutaric [19] finds the value of k to vary continuously with dilution, approaching 2.5 as the dilution approaches infinity.

From the density of the sol and water, together with the concentration determined analytically, Dumanskii calculates the density of the arsenic trisulfide in the particles, from Equation (3) above, to be 3.11.[57] By a similar procedure Burton and Currie [58] find the density of arsenic trisulfide in the colloidal state to be the same as the density in mass.

The original Einstein equation for the viscosity of a suspension of rigid spheres has been modified by Smoluchowski [59] for the viscosity, η_s, of a sol:

$$\eta_s = \eta_0 \left[1 + 2.5\phi \left\{ 1 + \frac{1}{kr_2\eta_0} \left(\frac{D\zeta}{2\pi} \right)^2 \right\} \right]$$

where k is the conductivity of the system; r, the radius of the particles; D, the dielectric constant; and ζ, the electrokinetic potential of the particles. Tendeloo [60] has used this equation with some success in measuring the mean size of the particles in different arsenic trisulfide sols.

Chemical Properties

Ozone acts on arsenic trisulfide sol giving arsenic acid.[61] Stannous chloride reduces it to As_2S_2, which is similar in color to antimony trisulfide; hence in qualitative analysis arsenic is sometimes mistaken for

[53] Compt. rend., **152**, 1382 (1911).
[54] Kolloid-Z, **7**, 301 (1910).
[55] Z. physik. Chem, **80**, 709 (1912).
[56] Kolloid-Z., **11**, 280 (1912).
[57] *Cf.* Wintgen: Kolloid-Beihefte, **7**, 251 (1915).
[58] Trans. Roy. Soc. Can., III **16**, 109 (1922).
[59] Kolloid-Z., **18**, 190 (1916).
[60] Kolloid-Z., **41**, 290 (1927).
[61] Riesenfeld and Haase: Z. anorg. Chem, **147**, 188 (1925).

antimony in the presence of tin.[62] Peskov [63] studied the velocity of solution of colloidal arsenic trisulfide in sodium hydroxide or sodium carbonate and found the process to be subject to the lyotropic influence of the cations of neutral salts in the order: $NH_4 < Li < Na < K < Rb < Cs$. The velocity of solution does not take place either as a purely heterogeneous or molecular process but appears to be a heterogeneous process modified by the large surface of the small particles and by Brownian movement.

If arsenic trisulfide sol is taken into the body in any way, it is precipitated in a granular form.[64] Injected intramuscularly or subcutaneously it appears in the tissues as minute granular particles. On intravenous injection, there is rapid coagulation which may result in small emboli in the capillaries, especially of the lungs. The sulfide produces a more marked pharmacological effect on the smallest lung capillaries and alveoli than any other organic or inorganic compound. Meneghetti suggests that for this reason non-lethal doses may have a therapeutic value in some diseases of the lungs. Traces of arsenic trisulfide sol have been found to increase liver autolysis, but higher concentrations inhibit the process.[65]

[62] Ehrenfeld: Ber., **40**, 3962 (1907).
[63] Kolloid-Z, **32**, 163, 238 (1923).
[64] Meneghetti: Biochem. Z., **121**, 1 (1921); Foá and Aggazzotti: **19**, 1 (1909).
[65] Ascoli and Izar: Biochem. Z., **6**, 192 (1907).

CHAPTER X

COLLOIDAL ARSENIC TRISULFIDE: STABILITY OF SOL

The hydrosol of arsenic trisulfide behaves for the most part as a typical hydrophobic sol. It therefore owes its stability primarily to the adsorption of the potential-determining S^{--} and HS^{-} ions derived from hydrogen sulfide, the stabilizing electrolyte. This chapter will deal with the various factors which influence the stability of the sol, especially the effect of foreign electrolytes.

Coagulation by Electrolytes

The Critical ζ-potential

The addition of electrolytes to sols usually lowers the electrokinetic or ζ-potential which is calculated from the migration velocity, u, of the particles moving under a potential H in a medium of viscosity η and dielectric constant D by means of Freundlich's [1] equation:

$$\zeta = \frac{4\pi\eta u}{HD} \tag{1}$$

Hydrosols. The concept of a critical ζ-potential, above which the sol is relatively stable and below which it coagulates rapidly, follows from observations of Powis [2] on negative arsenic trisulfide sol. In Table XVII are given the ζ-potentials at the surface of arsenic trisulfide particles when sufficient amounts of the several electrolytes are added to cause rapid coagulation. It is significant that the critical potential is the same in the presence of all multivalent cations, the coagulating ions for negative sols. For the univalent potassium ion, the calculated ζ-potential is much higher than for the multivalent ions. This is not a question of the univalence of potassium ion, as evidenced by some data of Briggs,[3] shown graphically in Fig. 29, in which the

[1] "Kapillarchemie," 2nd ed., 331 (1922).
[2] J. Chem. Soc., **109**, 734 (1916).
[3] J. Phys. Chem., **34**, 1326 (1930); *cf.* Ghosh: J. Chem. Soc., 2693 (1929).

TABLE XVII

CRITICAL ζ-POTENTIAL OF PARTICLES IN As_2S_3 SOL

Electrolyte	Concentration milliequivalents/l	ζ-potential millivolts
KCl	40 0	44
$BaCl_2$	1 0	26
$AlCl_3$	0 15	25
$Th(NO_3)_2$	0 20	27
$Th(NO_3)_2$	0 28	26
$Th(NO_3)_2$	0 40	24

mobility, rather than the ζ-potential calculated therefrom, is plotted against the electrolyte concentration for potassium chloride, new fuch-

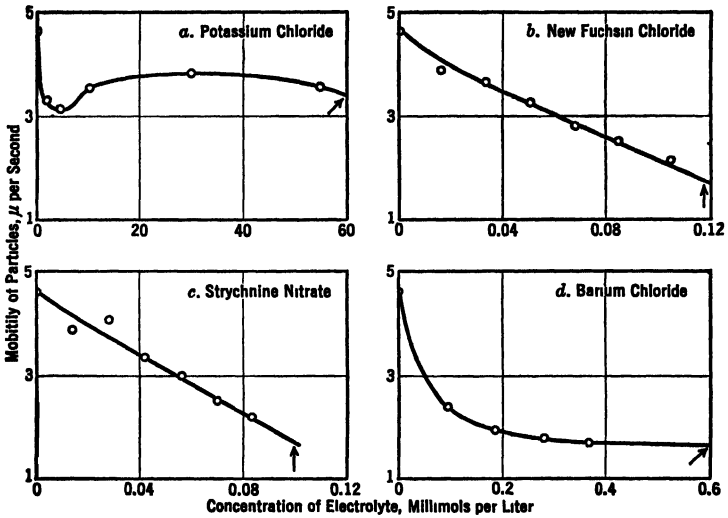


FIG. 29.—Effect of electrolytes on the mobility of the particles in arsenic trisulfide sol.

sin chloride, strychnine nitrate, and barium chloride. In this connection McBain[4] showed Equation (1) to be inadequate for calculating

[4] J. Indian Chem. Soc. (Ray Commemorative Volume), 67 (1933); *cf., however,* Audubert: J. chim. phys., **30**, 89 (1933); *also,* Muller: Kolloid-Beihefte, **28**, 257 (1928); (Vol. II, p. 68).

the ζ-potential of the particles and suggested the wisdom of using the *u*-value which gives a direct quantitative expression of all electrokinetic phenomena rather than the corresponding ζ-potential calculated by means of an equation which does not include all the variables. As would be expected, the mobility of the sol particles changes on dialysis.[5]

Referring to the arrows which mark the point of rapid coagulation it is apparent that the univalent dye and strychnine cations, and bivalent barium, cause coagulation at approximately the same mobility (or ζ-potential). On the other hand, the mobility at the coagulation point for potassium chloride is considerably higher than that for the electrolytes which coagulate in low concentration, and the course of the mobility-concentration curve is S-shaped. In some cases the mobility curve with salts of the KCl-type increases from the start to a maximum and then decreases;[6] in others, it decreases from the start;[7] and in still others, it decreases to a minimum and then increases.[8] With potassium ferrocyanide as precipitating electrolyte, coagulation takes place when the mobility is higher than that of the original sol.[6] Mukherjee and coworkers[8] found differences in the form of the curves depending on the method of preparation and the dilution of the sol.

Powis attributed the apparently anomalous behavior of electrolytes that coagulate in high concentrations to a salting-out effect which causes coagulation when the calculated ζ-potential is higher than it is for electrolytes which coagulate in low concentration. Kruyt[9] postulated a change in the dielectric constant to account for the unusual behavior of negatively charged sols toward salts with univalent cations of the KCl-type. With weak solutions of electrolytes it is permissible to assume that D is approximately the same as for water, but with stronger solutions D is lower than for pure water, giving a ζ-potential,

[5] Joshi, Barve, and Desai: Proc. Indian Acad. Sci, **4A**, 590 (1936).

[6] Kruyt and van der Willigen: Z. physik. Chem., **130**, 170 (1927).

[7] Freundlich and Zeh: Z. physik. Chem., **114**, 84 (1925); Mukherjee and Chaudhury: J. Indian Chem. Soc, **2**, 296 (1925); **4**, 493 (1927).

[8] Mukherjee, Chaudhury, and Bhattacharya: J. Indian Chem. Soc., **5**, 735 (1928); Mukherjee and Ganguly: **7**, 465 (1930); Mukherjee, Chaudhury, and Rajkumar: **10**, 26 (1933); Mukherjee: Nature, **122**, 960 (1928); Mukherjee and Chaudhury: Science and Culture, **1**, 111 (1935).

[9] Kruyt, Roodvoets, and van der Willigen: Colloid Symposium Monograph, **4**, 304 (1926); Kruyt and van der Willigen: Z. physik. Chem., **130**, 170 (1927); Kruyt and Briggs: Proc. Acad. Sci. Amsterdam, **32**, 384 (1929); Ivanitskaja and Proskurnin: Kolloid-Z., **39**, 15 (1926).

calculated from Equation (1), that is higher than it should be. In other words, the critical potential does not depend on a definite u-value but on the value of u/D. In accord with this, it has been found [10] that in very dilute solutions of potassium chloride, for example, the value of D decreases slightly, then immediately increases as the concentration of the solution increases, the minimum being at a concentration of 4–8 millimols per liter. This would account for the S-shape of the mobility-concentration curve for potassium chloride, as found by Briggs.

Mukherjee and coworkers [8] and Ghosh [11] believe that an increase in dielectric constant alone would not account for the observed behavior of salts of the KCl-type with arsenic trisulfide sol unless an improbably high value were assigned to it. The anomalous behavior may be due in part to the stabilizing action of adsorbed chloride and ferrocyanide ions which opposes the precipitating action of potassium ion. It is further assumed that the force of attraction between the particles may vary inversely with the distance according to a power higher than that involved in the electric repulsion due to the presence of the electric double layer.[11]

Because of the anomalous effect of certain coagulating electrolytes on the mobility of negative sols, Mukherjee and coworkers contend that one should not speak of a critical mobility or a critical ζ-potential This point of view seems a bit extreme under the circumstances. In most cases electrolytes effect coagulation at a critical mobility or ζ-potential. The fact that we do not know enough at present to interpret adequately the behavior with certain salts that coagulate in relatively high concentrations is no reason to abandon the whole concept of a critical mobility or ζ-potential. Indeed, for some reason the anomalous behavior seems to be confined to negative sols. Thus Ghosh [12] found that a positive ferric oxide sol becomes instable when the potential falls to about 32 millivolts using such widely different electrolytes as potassium chloride, sulfate, oxalate, and ferricyanide; sodium hydroxide; and aniline sulfate (*cf.* also p. 419).

Organosols. Bikerman [13] investigated the change in the ζ-potential on adding electrolytes to organosols of arsenic trisulfide in nitrobenzene

[10] Furth: Physik Z., **25**, 676 (1924); Pechhold: Ann Physik, **83**, 427 (1927); Walden and Werner: Z. physik. Chem., **129**, 389 (1927); Hellman and Zahn· Physik. Z., **27**, 636 (1926).

[11] Ghosh: J Chem Soc., 2693 (1929); *cf* Briggs· J Phys. Chem, **34**, 1326 (1930).

[12] J. Chem. Soc., 2693 (1929).

[13] Z. physik. Chem, **115**, 261 (1925).

and ethyl acetoacetate. Some observations with two ethyl acetoacetate sols are given in Table XVIII and shown graphically in Fig. 30. It will

TABLE XVIII

EFFECT OF ELECTROLYTES ON THE ζ-POTENTIAL OF THE ARSENIC TRISULFIDE PARTICLES IN ETHYL ACETOACETATE ORGANOSOL

Electrolyte	Concentration millimols/l	ζ-potential millivolts
$FeCl_3$	0 00123	85
	0 0036	80
	0 038	52
	0 110	53
	0 422	40
	0 700 (coagulation value)	30
$Cu(C_6H_9O_3)_2$	0 0011	78
	0 0113	65
	0 220	53
	0 660	38
	0 900 (coagulation value)	31
$N(C_3H_7)_4I$	0 134	78
	1 280	46
	3 0 (approximate coagulation value)	

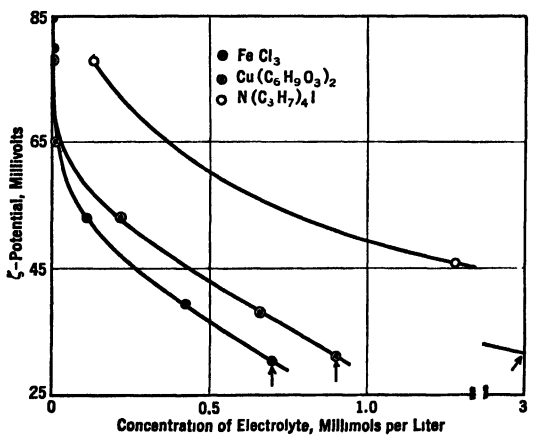


FIG 30.—Effect of electrolytes on the ζ-potential of arsenic trisulfide particles dispersed in ethyl acetoacetate.

be seen that a given molar concentration of electrolytes decreases the ζ-potential of the particles in the order: $FeCl_3 > Cu(C_6H_9O_3)_2 > N(C_3H_7)_4I$. The precipitation value (indicated by an arrow) in millimols per liter for $FeCl_3$ is 0.7; for $Cu(C_6H_9O_3)_2$, 0.9; and for $N(C_3H_7)_4I$, in the neighborhood of 3. If all the values were given in equivalents, the curve for the iron salt would be above that for the copper salt and the precipitation value for the former would be below that for the latter in accord with Schulze's valency rule. The critical ζ-potential is in the neighborhood of 30 millivolts for all electrolytes.

A comparison of the data obtained with ethyl acetoacetate and nitrobenzene organosols shows that the critical ζ-potential calculated from Equation (1) is practically independent of the dielectric constant of the medium. Thus the values of D for the two media differ by 130%, whereas the difference in the calculated value of ζ is only 20%. These results furnish additional support to the view that the ζ-potential, instead of the charge on the surface of the particles, determines sol stability (*cf.* p. 419).

Precipitation Values of Electrolytes

Procedure. Several methods have been employed from time to time for determining the relative precipitating power of electrolytes. Since the process is transitory, it is necessary to compare the electrolyte concentrations which produce the same velocity of coagulation. The rate of coagulation has been followed by means of viscosity measurements on alumina sol;[14] by colorimetric observations on gold sol;[15] and Congo rubin sol;[16] with a spectrophotometer on gold sol and arsenic trisulfide sol;[17] and with a turbidity meter on arsenic trisulfide sol.[18] In an arsenic trisulfide sol, the viscosity-time curve on adding an electrolyte such as potassium chloride first falls and then rises rapidly as the coagulation proceeds.[19] The times for attaining a given viscosity might be taken as a measure of the coagulating power of different electrolytes. For the most part, however, investigators compare the concentrations which just cause complete precipitation in a

[14] Gann: Kolloid-Beihefte, **8**, 64 (1916).

[15] Hatschek: Trans. Faraday Soc, **17**, 499 (1921).

[16] Lüers: Kolloid-Z., **27**, 123 (1920).

[17] Mukherjee and Majumdar: J. Chem. Soc., **125**, 785 (1924); Boutaric and Vuillaume: Compt. rend., **172**, 1293 (1921).

[18] Ghosh: J. Indian Chem. Soc., **9**, 591 (1932).

[19] Joshi and Viswanath: J. Indian Chem. Soc, **10**, 329; Joshi and Menon: 599 (1933).

definite period of time, not less than 2 hours. As Freundlich [20] has shown, these precipitation values have a definite meaning from the standpoint of coagulation since with certain concentrations there always exists a constant maximum coagulation velocity, the velocity of so-called instantaneous coagulation,[21] and hence the coagulations are comparable when this velocity is attained.

In determining the precipitation values of sols a uniform procedure as regards stirring should be followed. Thus, if an arsenic trisulfide sol is shaken continuously, appreciable flocking will result in a given time with a concentration of electrolyte that will cause no flocking whatsoever without stirring.[22] It has been observed repeatedly [23] that the critical concentration of electrolytes does not cause agglomeration of the particles into a clump unless the mixture is shaken. Apparently what happens is that the potential on the particles is reduced to the critical value, but, instead of agglomerating into a clump, the individual particles with their film of adsorbed water coalesce to a loose jelly structure that is readily broken up by stirring. If a concentration of electrolyte close to the critical value is used and the sol is allowed to stand quietly for a day or two, the surface of the precipitate as it settles appears to be a fairly strong, translucent, mobile film, strikingly similar in appearance to that of a copper ferrocyanide membrane. Since the stability of arsenic trisulfide sols decreases on aging [24] it is advisable to obtain all the values of a given series within a comparatively short time interval if comparable values are desired.

Schulze's Rule. Some observations of Freundlich [25] on the precipitation of arsenic trisulfide sol are given in Table XIX. Except for the univalent organic ions, the salts with ions of the same valence fall in fairly well-defined groups, the univalent ions precipitating in highest concentration and the trivalent ions in lowest concentration, in accord with the rule proposed by Schulze [26] from similar observa-

[20] Kolloid-Z., **23**, 163 (1918).

[21] Smoluchowski: Z. physik. Chem., **92**, 129 (1917).

[22] Freundlich and Basu: Z. physik. Chem, **115**, 204 (1925); Freundlich and Kroch: **124**, 155 (1926); Boutaric and Vuillaume: Compt. rend., **174**, 1351 (1922); *cf.* Wo Ostwald: Kolloid-Z, **41**, 71 (1927).

[23] Weiser: Colloid Symposium Monograph, **4**, 369 (1926).

[24] Freundlich and Schucht: Z. physik. Chem., **80**, 566 (1912); Ghosh and Dhar: Kolloid-Z., **36**, 134 (1925); Krestinskaja and Jakowlewa: **44**, 141 (1928); Krestinskaja: **66**, 58 (1934).

[25] Z. physik. Chem., **73**, 385 (1910); *cf., also,* Schilow: **100**, 425 (1922); Bach: J. chim. phys., **18**, 46 (1920).

[26] J. prakt. Chem., (2) **25**, 431; **27**, 320 (1883).

TABLE XIX

PRECIPITATION VALUES OF ELECTROLYTES FOR ARSENIC TRISULFIDE SOL

Electrolyte	Precipitation value millimols/l	Electrolyte	Precipitation value millimol/l
$KC_2H_3O_2$	110 0	Morphine chloride	0 425
$KCHO_2$	86 0	Crystal violet	0 165
LiCl (*a*) . . .	58 4	New fuchsin .	0 114
NaCl (*a*)	51 0	$MgCl_2$ (*b*)	0 717
KNO_3 (*a*)	50 0	$MgSO_4$	0 810
KCl (*a*)	49 5	$CaCl_2$ (*b*)	0 649
$K_2SO_4/2$..	65 6	$SrCl_2$ (*b*)	0 635
NH_4Cl (*a*) .	42 3	$BaCl_2$ (*b*) .	0 691
HCl	30 8	$Ba(NO_3)_2$ (*b*)	0 687
$H_2SO_4/2$	30 1	$ZnCl_2$ (*b*)	0 685
Guanidine nitrate	16 4	$UO_2(NO_3)_2$ (*b*)	0 642
Strychnine nitrate	8 0	Quinine sulfate	0 240
Aniline chloride	2 52	$AlCl_3$. .	0 093
		$Al(NO_3)_3$	0 095
		$Al_2(SO_4)_3/2$	0 096
		$Ce(NO_3)_3$.	0 080
		$Ce_2(SO_4)_3/2$	0 092

tions on arsenic trisulfide and antimony trisulfide sols. It should be emphasized, however, that ions of the same valence do not behave alike and that the behavior of the alkaloid and dye cations follows no rule as to valence. Although the exceptions to Schulze's rule are so numerous that it should be looked upon merely as a qualitative statement Freundlich and Schucht [27] have used the principle with some success in confirming the valence of certain ions. Thus the results recorded in Table XX indicate the trivalence of the rare earths and of indium. In a similar way, Galecki [28] showed that beryllium behaved like a bivalent metal as we now know that it should. The similarity in precipitating power of multivalent elements having the same charge is more striking in Table XX than in Table XIX, probably because of the marked similarity which exists among the rare-earth elements. Burton and Bishop [29] report that ceric nitrate behaves like a salt with a trivalent cation and not like one with a tetravalent cation. Since

[27] Z. physik. Chem., **80**, 564 (1912).
[28] Z. Elektrochem., **14**, 767 (1908).
[29] J. Phys. Chem., **24**, 701 (1920).

TABLE XX

PRECIPITATION VALUES OF SOME LESS COMMON ELECTROLYTES FOR ARSENIC TRISULFIDE SOL

Electrolyte	Precipitation value millimol/l	Valence of cation
Strontium nitrate	0 54	2
Xantho cobalt sulfate	0 55	2
Purpureo cobalt chloride	0 55	2
Aluminum sulfate	0 075	3
Yttrium chloride	0 073	3
Cerium nitrate	0 075	3
Neodymium ammonium nitrate	0 080	3
Praseodymium ammonium nitrate	0 079	3
Samarium chloride	0 083	3
Europium chloride	0 092	3
Gadolinium chloride	0 080	3
Dysprosium chloride	0 086	3
Erbium chloride	0 064	3
Indium nitrate	0 082	3
Luteo cobalt chloride	0 082	3
Roseo cobalt chloride	0 120	3

$Ce(NO_3)_4$ is said to be non-existent, it is probable that they were using the trivalent salt which is sometimes erroneously called ceric nitrate. It is interesting that the slow transformation of bivalent purpureo cobalt chloride to the trivalent roseo salt can be followed by the gradual increase in precipitating power.

Traube's Rule in Coagulation. From investigations on the coagulation of arsenic trisulfide sols by different amine salts, Freundlich [30] found the precipitating power to increase regularly with the addition of CH_2 groups in accord with Traube's rule, which states that the capillary activity, that is, the lowering of the surface tension of water and the adsorption by solid adsorbents, increases regularly with the addition of CH_2 groups in an homologous series. This is illustrated by observations on two different sols prepared in the same way and of approximately the same concentration: (*a*) 0.475 g/l, and (*b*) 0.465 g/l (Table XXI). The addition of each successive pair of CH_2 groups causes a marked falling off in the precipitation value. This

[30] Freundlich and Birstein· Kolloid-Beihefte, **22**, 95 (1926); Freundlich and Slottman: Z. physik. Chem., **129**, 305 (1927).

TABLE XXI

COAGULATION OF ARSENIC TRISULFIDE SOLS BY HOMOLOGOUS AMINE CHLORIDES

Electrolyte	Sol *a*		Sol *b*	
	Precipitation value, *x* millimols/l	Activity factor x_n/x_{n+1}	Precipitation value, *x* millimols/l	Activity factor x_n/x_{n+1}
NH_4Cl . . .	35 00	..	51 0	.
$C_2H_5NH_3Cl$.	18 20	1.9	17 5	3 0
$(C_2H_5)_2NH_2Cl$. .	9 96	1 8	5 3	3 3
$(C_2H_5)_3NHCl$	2 78	3 5	1 5	3 5
$(C_2H_5)_4NCl$	0 89	3 2	0 85	1 8

decrease is probably not directly proportional to the number of CH_2 groups, but the variation from a constant ratio in a series is no greater than the variation between one sol and another. Similar observations were made on a hydrous ferric oxide sol with a series of sodium salts of fatty acids. Also, the difficultly soluble sodium fumarate was found to have a much higher coagulating power for ferric oxide sol than the more readily soluble isomeric sodium malonate. This accords with the usual view that the least soluble substance is the most capillary active, that is, the most strongly adsorbed.

Ostwald's Activity Coefficient Rule. Because of the limitations of the rules of electrolyte coagulation which attempt to formulate the conditions for reducing the ζ-potential on the particles to a critical value, Ostwald [31] introduced the principle that the dispersion medium rather than the micelles should be in a corresponding (in the simplest case identical) physical chemical state for coagulation to take place. It is argued that coagulation should take place at the same activity coefficient of the precipitating ion (f^+ for negative sols and f^- for positive sols), irrespective of the salt employed. For negative sols such as arsenic trisulfide the cation activity coefficient is defined, in accordance with the Debye-Hückel theory, by a relation of the form

$$-\log f^+ = 0.5\,(z^+)^2\sqrt{u/n^+}$$

in which z is the valence of the cation, n^+ the number of cations in the molecule (this is not in the equation of Debye and Hückel), and u is the ionic strength which is given by the expression

$$u = 0.5\,[m^+\cdot(z^+)^2 + m^-\cdot(z^-)^2]$$

[31] Kolloid-Z., **73**, 301 (1935).

where m^+ and m^- are the molar concentrations (molarities) of the cation and anion, and z^+ and z^- are the valences of the respective ions in the coagulating electrolyte. As an illustration of the applicability of the rule $f^+ =$ constant, we may examine Table XXII which

TABLE XXII

COAGULATING POWER AND ACTIVITY COEFFICIENT OF ELECTROLYTES

Salt type	No. of each type	Salts considered from Table XIX	Precipitation value mol/l (average)	Activity coefficient of cation (f^+)
1–1	5	Salts marked (*a*)	0 0502	0 77
1_2–2	1	$K_2SO_4/2$	0 0656 (0 0328)*	0 78 (0 83)*
2–1_2	7	Salts marked (*b*)	0 000672	0 82
2–2	1	$MgSO_4$	0 000810	0 77
3–1_3	2	$AlCl_3$; $Al(NO_3)_3$	0 000093	0 78
3_2–2_3	1	$Ce_2(SO_4)_3$	0 000092	0 82

* For the precipitation value of $K_2SO_4/2$ Ostwald used 0.0328 mol/l instead of Freundlich's value, 0.0656.

Ostwald constructed from Freundlich's data [82] in Table XIX. The figures under the heading "Salt Type" are the valences of the respective ions. Other tables of a similar nature were obtained from coagulation data on arsenic trisulfide sol and other sols, by various investigators. A comparison of the data on arsenic trisulfide sol shows f^+ to be constant within a few per cent for the work of a given investigator and to vary only between 0.68 and 0.83 when applied to the work of different investigators. This might seem to establish the general validity of the rule; but its limitations call for special attention. In the first place the rule is admittedly applicable only to approximately neutral inorganic salts. Confining ourselves to Tables XIX and XXII, we see that Ostwald has chosen to omit the simple organic salts, the dyes, the alkaloids, sulfuric and hydrochloric acid, and ceric nitrate, because the inclusion of any one of them would make the rule look less satisfactory. Omitting the organic compounds may be justifiable, but it is not obvious why some of the inorganic compounds should be omitted. In other tables of data, sulfates of bivalent cations like magnesium sulfate give values of f^+ which are much too low to obey the rule. This is explained by the tendency of the ions to form complex

[82] *These data are taken from* Freundlich: Z. physik. Chem., **73**, 385 (1910) *and not* **44**, 135 (1903), *as stated by Ostwald.*

salts with arsenic trisulfide. But magnesium sulfate fits in all right in Table XXII and is therefore included. For the five salts of the type 1–1 that are lumped together, there is a maximum variation of 16% above and below the mean coagulation value. It is questionable whether it is permissible to average values that vary so widely. Potassium formate (0.086) and hydrochloric acid (0.031) might have been averaged with the other five without affecting the result materially, but Ostwald very properly did not do so(*cf.* p. 188). In calculating the f^+-value for potassium sulfate, Ostwald used 0.0328 mol/l for the precipitation value of $K_2SO_4/2$ instead of Freundlich's value of 0.0656 mol/l. In spite of this, the calculated f^+-value was in line with the others. One must accept with reservations any rule that will iron out data that are in error by 100%. Finally, there appears to be no reason why the f^+-values of univalent precipitating ions should be the same as the f^+-values of multivalent precipitating ions since only a small percentage of univalent ions is adsorbed at the precipitation value whereas a large percentage of most multivalent ions is adsorbed at the precipitation value.

Based on the above principles a new valency rule was formulated which requires that the reciprocal of the coagulating molarities for the valence types 1–1, 1_2–2, 1_3–3, 1_4–4, 2–1_2, 2–2, 3–1_3, 3_2–2_3, 3–3, 4–1_4, 6–1_6 stand in the ratio 1 : 1.5 : 2 : 2.5 : 48 : 64 : 486 : 608 : 729 : 2560 : 27,200. That this is not in agreement with observed results may be due in part to inaccuracies in the data but is probably due chiefly to some neglected factors. The averages for the many investigations on arsenic trisulfide sol agree only in order of magnitude with this set of ratios. In certain special cases the above valency rule reduces to an earlier rule of Freundlich and Ostwald (p. 207).

Effect of Concentration of Sol. The precipitation value of a given arsenic trisulfide sol changes with the concentration of the sol, a fact observed first by Mukopadhyaya.[33] Later Kruyt and van der Spek[34] showed that, on dilution, the precipitation value of potassium chloride increased, that of barium chloride decreased slightly, and that of aluminum sulfate decreased greatly. This was confirmed and extended by Burton and coworkers,[29, 35] who formulated the rule that, in general, the precipitation value of univalent precipitating ions increases with the dilution; that of bivalent ions is almost constant and independent

[33] J. Am. Chem. Soc., **37**, 2024 (1915).

[34] Kolloid-Z, **25**, 3 (1919); Mukherjee and Sen: J. Chem. Soc., **115**, 462 (1919); Mukherjee and Papaconstantinou: **117**, 1569 (1920).

[35] Burton and MacInnes: J. Phys. Chem., **25**, 517 (1921).

of the sol concentration; and that of trivalent ions varies almost directly with the sol concentration. Weiser and Nicholas [36] showed that Burton's rule is not generally applicable since with many sols, especially those of the hydrous oxides, the precipitation value of electrolytes decreases with dilution of sol irrespective of the valence of the precipitating ion.

The results of some observations of Weiser and Nicholas are shown graphically in Fig. 31 in which the percentage concentration of sol is plotted against the ratio of each precipitation value for a given electrolyte to that of the strongest colloid (6.7 g/l). Three factors

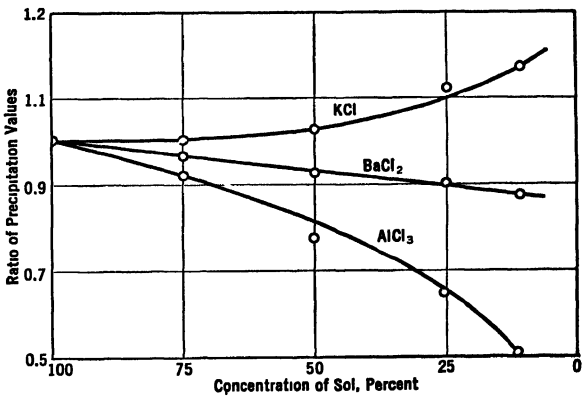


FIG 31.—Effect of the concentration of arsenic trisulfide sol on its stability toward electrolytes.

appear to determine the effect of dilution of sol on the precipitation value: (*a*) the smaller number of particles in the weaker sol requires less electrolyte to lower the ζ-potential to the critical value; (*b*) the decreased chance of collision requires a lower potential and hence more electrolyte to effect coagulation in a given time; [37] and (*c*) the stabilizing effect of the ion having the same charge as the sol.[38] Of these three factors, (*a*) predominates with electrolytes containing strongly adsorbed multivalent precipitating ions that cause precipitation in low

[36] J. Phys. Chem., **25**, 742 (1921); Takamatsu: Kolloid Z., **38**, 229 (1926); Rabinovich and Dorfmann, Z. physik Chem., **131**, 313 (1927); Boutaric and Perreau: J chim. phys, **24**, 498 (1927); *cf.* Pauli and Laub: Kolloid-Z., **78**, 295 (1937).

[37] Kruyt and van der Spek: Kolloid-Z., **25**, 3 (1919).

[38] Weiser and Nicholas: J. Phys. Chem., **25**, 742 (1921).

concentrations; (*b*) can be disregarded as a rule; and (*c*) is of primary importance if the precipitation concentration is high, as is usual with univalent precipitating ions. The tendency for the precipitation value of electrolytes with univalent cations to increase with dilution is indicated by a rise in the mobility of the particles as a given sol is diluted. This effect cannot be due to arsenious acid resulting from increased hydrolysis of arsenic trisulfide in the more dilute sol since the addition of arsenious acid has a sensitizing effect by lowering the mobility.[39] Rossi and Marescotti [40] attribute the difference in the be-

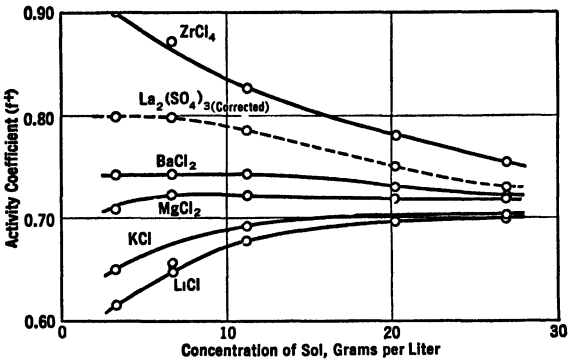


FIG. 32.—Influence of the concentration of arsenic trisulfide sol on the activity coefficient of cations at the precipitation value.

havior of arsenic trisulfide sol from that of ferric oxide sol to the greater increase in the degree of dispersity which the former undergoes on dilution.[41]

Ostwald [42] has applied his activity coefficient rule to the effect of dilution on the coagulation value. The $f+$-values were calculated from the molar precipitation values for various dilutions of sol and these were plotted against the sol concentrations. As an illustration, Ostwald's data calculated from Burton and MacInnes' observations on a sol containing initially 27 g As_2S_3/l, are given in Fig. 32. The data

[39] Mukherjee and Ganguly: J. Indian Chem. Soc, **7**, 465 (1930); Mukherjee, Chaudhury, and Palit: **10**, 27, 713 (1933); Mukherjee: Kolloid-Z., **53**, 159 (1930).

[40] Gazz. chim. ital., **59**, 313 (1929); **60**, 993 (1930).

[41] *Cf., also,* Gerasemov and Urzhumskii: J. Russ. Phys.-Chem. Soc., **61**, 393 (1929).

[42] Kolloid-Z., **75**, 39 (1936); Wannow and Hoffmann: **80**, 294; Ostwald: 304 (1937).

for aluminum chloride do not fit in for some unknown reason; those for ceric nitrate do not fit for the obvious reason that there is no such compound as $Ce(NO_3)_4$ (*cf.* p. 189). The recorded values for lanthanum sulfate were multiplied by 2 on the presumption that Burton and MacInnes had worked with an equivalent instead of a molar solution. From these and similar findings with more dilute sols used by Kruyt and van der Spek and Weiser and Nicholas, Ostwald concluded that the activity coefficient rule is a limiting rule which holds only at high concentrations of sol. Hence the course of the precipitation value-sol concentration curve is always determined by the magnitude of the increasing divergence from the constant $f+$-value on dilution of sol. Since the $f+$-values diverge so widely with a sol as dilute as 3.63 g As_2S_3/l (Fig. 32) it is obvious that the fairly constant $f+$-values recorded in Table XXII are quite accidental since Freundlich's sol contained but 1.8 g/l.

In an important investigation, the results of which were published while this volume was in press, Wannow and Hoffmann [42] determined the precipitation value of KCl, $MgCl_2$, and $LaCl_3$ on arsenic trisulfide sols varying in concentration from 18.7 to 0.018 g As_2S_3/l. The $f+$-concentration of sol curves for the three cations were found to cut each other at a concentration of 4.7 g As_2S_3/l. The theoretical significance of Wannow and Hoffmann's results were discussed by Ostwald.[42]

Effect of Anions on the Precipitation Value. Although it is often assumed that one is justified in neglecting the effect of anions in the precipitation of negative sols and of cations in the precipitation of positive sols, it is evident that this will be true only if the adsorption of the ion having the same charge as the sol—the stabilizing ion—is negligible either because of its nature or the dilution. Although this effect may be slight in certain cases it is quite marked in others as illustrated by some observations of Freundlich,[43] Ghosh and Dhar,[44] and Weiser and Nicholas [38] summarized in Table XXIII. Pauli and Valko [45] suggest that the activity rather than the concentration of potassium ion in the several salts should be compared. This has been done by Ostwald, and his $f+$-values are included in the table. These values are about the same with the chloride and sulfate but they are lower with the ferrocyanide, indicating that the anion may influence the precipitating power of an electrolyte independent of its effect on

[43] Z. physik. Chem., **44**, 152 (1903).
[44] Kolloid-Z, **36**, 129 (1925).
[45] "Elektrochemie der Kolloide," 193 (1929).

the activity of the cation. With potassium citrate containing the strongly stabilizing citrate ion, the calculated $f+$-values are much lower; but it is probably not permissible to apply the Debye-Huckel theory to this salt.

TABLE XXIII

PRECIPITATION VALUE OF POTASSIUM SALTS FOR ARSENIC TRISULFIDE SOLS

[Precipitation values (x) in mol/l of cation]

Electrolyte	Sol 1 1 8 g/l		Sol 2 3 7 g/l		Sol 3 5 0 g/l	
	x	f^+	x	f^+	x	f^+
KCl	0 0495	0 77	0 085	0 72	0 0332	0 81
$K_2SO_4/2$	0 0656	0 78	0 100	0 73	0 0435	0 82
$K_4Fe(CN)_6/4$. .			0 185	0 68	0 0712	0 79
$K_3C_6H_5O_7/3$	0 2400	0 63	0 270	0 62		..

Mukherjee and Chaudhury[46] estimated the time required for the same concentration of various salts to make the sol so cloudy that a heated filament a definite distance away was just obscured. From the results obtained, it was concluded that the influence of anions is negligible except in the case of the so-called complex ions like benzoate, ferrocyanide, and salicylate which exert a marked effect. Actually, their data show the precipitating power of iodate and nitrate to be less than that of chloride and bromide. Oxalate admittedly has a lower precipitating power than sulfate which can hardly be attributed to difference in the complexity of the ions. It appears, therefore, that Mukherjee's observations support rather than refute the contention that the effect of the anion cannot be neglected, even though his procedure probably gives a less accurate measure of precipitating power than carefully determined precipitation values. Following the same general method of procedure Ostwald[47] demonstrated the effect of anions by determining the rate of precipitation of various organic and inorganic acids as a function of their pH values. The pH-time curves do not coincide, indicating that the anions have varying stabilizing effects or that the different ions or molecules have varying dehydrating powers.

[46] J. Chem. Soc., **125**, 794 (1924).

[47] Kolloid-Z., **40**, 201 (1926); *cf.* Boutaric and Perreau: Bull. sci. acad. roy. Belg., **14**, 666 (1928).

Acclimatization. Arsenic trisulfide sol like hydrous ferric oxide sol (Vol. II, p. 72) requires less electrolyte to cause precipitation when added all at once than when added stepwise through a relatively long interval of time.[48] For example,[49] on rapid addition, 2.05 cc of 0.02 *N* $SrCl_2$ and 2.50 cc of 0.5 *N* KCl were required to coagulate 20 cc of As_2S_3 sol whereas, on slow addition of the electrolytes in 0.1-cc portions over a period of approximately 36 hours, the amounts required were 2.50 and 2.70 cc, respectively. This phenomenon is known as "acclimatization," meaning that the colloid becomes acclimated to its surroundings when the electrolyte is added slowly so that more is required to produce a given result. In the author's opinion the term is a misnomer. Sols which exhibit this behavior usually undergo fractional precipitation to a certain extent during the stepwise addition of electrolyte.[50] This fractional precipitation not only removes electrolyte from solution by adsorption but also alters the stability of the sol by decreasing the concentration. From this point of view, the excess of electrolyte required for a given slow rate of precipitation is determined by (*a*) the extent to which the sol undergoes fractional coagulation, (*b*) the adsorbing power of the precipitate, (*c*) the adsorption of the precipitating ions, and (*d*) the effect of dilution of sol on the precipitation value (see above). Krestinskaja and Jakowlewa[51] attribute the so-called acclimatization of arsenic trisulfide sol toward barium chloride to irreversible hydrolysis of the salt giving arsenious acid and hydrogen sulfide which react with barium to give slightly dissociated, slightly soluble salts in larger amounts the more slowly the electrolyte is added. The objection to this explanation is that it will not hold for potassium chloride.

Charge Reversal: Irregular Series. Electrolytes with strongly adsorbed ions which precipitate in low concentrations frequently reverse the charge at concentrations above the precipitation value, and at still higher concentrations, precipitate the reversed sol once more (Vol. I, pp. 88, 126, 191). Charge reversal and the phenomenon of the so-called irregular series were observed by Lottermoser and May[52] with arsenic trisulfide sol using aluminum chloride, ferric chloride, and thorium

[48] Freundlich: Z physik. Chem, **44**, 143 (1903); *cf.* Dumanskii and Solin: Kolloid-Z, **59**, 314 (1932).

[49] Weiser: J. Phys. Chem, **25**, 399 (1921).

[50] *Cf.* Burton and Annetts: J. Phys. Chem., **35**, 48 (1931); Colloid Symposium Monograph, **8**, 48 (1931).

[51] Kolloid-Z, **44**, 141 (1928); *cf* Krestinskaja: **74**, 45 (1936).

[52] Kolloid-Z., **58**, 168 (1932).

nitrate as precipitating electrolytes. Boutaric and Semelet [53] failed to get a charge reversal with thorium nitrate, probably because they used too strong a sol. It is necessary for charge reversal not only for the reversing ion to be strongly adsorbed but also for the coagulation velocity to be sufficiently slow to avoid coagulation before the reversal takes place. Since the velocity of coagulation drops with dilution, it is possible to get charge reversal without coagulation with a dilute sol and coagulation without charge reversal with a more concentrated one.

Freundlich and Buchler [54] studied the charge-reversing property of a number of dyes and alkaloid hydrochlorides that have a high precipitating power on arsenic trisulfide sol. The results of some of their observations are shown in Table XXIV, in which $P-$ is the precipitation values of the dyes and alkaloids for the original negative

TABLE XXIV

CHARGE REVERSAL OF ARSENIC TRISULFIDE SOL BY DYES AND ALKALOIDS

Basic dye or alkaloid	$P-$	C_{max}	$P+$
Methyl green	0 02	1 0	9 5
Malachite green	0 05	1 0	35 0
Methylene blue	0 10	2 0	40 0
Chrysoidin	0.25	2 5	3 0
Crystal violet	1 3	3 0	3 0
Vuzin	0 006	0 06	30 0
Eucuprin	0 007	0 10	15 0
Quinine	0 004	0 12	5 0
Hydroquinine	0 010	0 26	5.0
Optochin	0 010	0 24	4.0

sol, C_{max} is the concentration which gives the maximum positive ζ-potential for the reversed sol, and $P+$ is the precipitation value of sodium or potassium chloride for the reversed sol, all in millimols per liter. In general the most strongly adsorbed cations give a reversed sol with the highest positive ζ-potential and with the greatest stability. Ostwald [55] has attempted to apply "activity coefficient rules" to the charge-reversal process with limited success.

[53] Boutaric and Semelet: J. chim. phys., **26**, 195 (1929).
[54] Kolloid-Z., **32**, 305 (1923).
[55] Kolloid-Z., **75**, 297 (1936).

It is of interest that the charge on arsenic trisulfide organosols can be reversed like that on hydrosols by adding an excess of a salt with a strongly adsorbed cation.[56] Thus a nitrobenzene sol containing 0.6 g As_2S_3/l is precipitated by 0.11 millimol $FeCl_3$/l; but 2.8 millimols $FeCl_3$/l gives it a charge of +55 millivolts.

In the light of the above observations and the further one that stable sols may be obtained in highly concentrated electrolytes (p. 174), it would follow theoretically that three zones of stability and three zones of instability may exist for a given sol with a single electrolyte in varying concentrations.[57]

Action of Non-electrolytes

The addition of non-electrolytes to sols usually decreases their stability toward electrolytes. The sensitization is attributed by Ostwald [58] and Cassuto [59] to a decrease in the dielectric constant of the medium. In line with this, Keeser [60] found arsenic trisulfide sol to be stabilized by the addition of urea and glycocoll both of which increase the dielectric constant of water.[61] Freundlich [62] suggests that the sensitization results from the lowering of the charge by adsorption on their surface of the organic non-conductor, which has a dielectric constant appreciably lower than that of water. Thus, the charge e on a particle is given by

$$e = \frac{\zeta D r(r + d)}{d} \qquad (2)$$

where ζ is the potential difference of the double layer at the surface of a spherical particle of radius r, D the dielectric constant, and d the thickness of the double layer. From this, it follows that a decrease in D will lower e and, hence, the precipitation value.

The dielectric constant of the non-electrolyte is not the only factor which influences the stability since sugar apparently acts as a stabilizer for sols [63] and one is not justified in ascribing the difference between alcohol and sugar to the dielectric constant. That sugars are adsorbed

[56] Bikerman: Z. physik. Chem., **115**, 261 (1925).
[57] Ostwald and Wannow: Kolloid-Z., **76**, 159 (1936).
[58] "Grundriss der Kolloidchemie," 441 (1909).
[59] "Der Kolloide Zustand der Materie," 152 (1913).
[60] Biochem. Z., **157**, 166 (1925); *cf.* Ghosh and Dhar: J. Phys. Chem., **29**, 668 (1925).
[61] Furth: Ann. Physik, **70**, 63 (1923).
[62] "Kapillarchemie," 2nd ed., 637 (1922).
[63] Ghosh and Dhar: J. Phys. Chem., **29**, 668 (1925).

by sulfide sols is evidenced by a loss in rotatory power when they are dissolved in the sols instead of in water.[64] In certain cases, the variation in adsorption with concentration of sugar can be formulated quite accurately by the Freundlich equation.[65]

Kruyt and van Duin [66] found the effect of non-electrolytes on the precipitation value of electrolytes for arsenic trisulfide sol to be determined by the nature of the precipitating ion. with univalent and trivalent ions, it was lowered; and with bivalent ions it was raised. For any given electrolyte, the change in precipitation value was independent of the dielectric constant of the non-electrolyte employed. The effect of the non-electrolyte is determined to some extent by the amount present. For example, if one dilutes an arsenic trisulfide hydrosol with propyl alcohol or the propyl alcosol with water, the stability of the sol toward calcium nitrate is greatest when the propyl alcohol content is approximately 25%.[67]

From a study of this behavior in the author's [68] laboratory the sensitizing action of non-electrolytes was attributed, at least in part, to the displacing of a stabilizing ion or the cutting down of the adsorption of a precipitating ion. These two actions are antagonistic, and so the precipitation value may be increased, decreased, or remain unchanged in the presence of a non-electrolyte. It was found, for example, that the adsorption of barium ion is cut down by the presence of phenol and the precipitation value is increased by the presence of phenol. This means that the sol is sensitized in the sense that less barium must be adsorbed to reduce the potential to the coagulation point; the higher precipitation value in the presence of phenol results from the cutting down of the adsorption of barium by the non-electrolyte.

In general the influence of foreign non-electrolytes on the stability of lyophobic sols can be accounted for at least qualitatively by considering:[69] the effect on (1) the dielectric constant of the medium, (2) the viscosity, (3) the degree of ionization of the electrolytes present, and (4) the selective adsorption of the precipitating and stabilizing

[64] Bhatnagar and Shrivastava: J. Phys. Chem., **28**, 730 (1924).

[65] Prasad, Shrivastava, and Gupta: Kolloid-Z, **37**, 101 (1925)

[66] Kolloid-Beihefte, **5**, 270 (1914); *cf., also,* Boutaric and Semelet: Rev. gén colloïdes, **4**, 268 (1926); Lachs and Chwalinski: Z. physik. Chem., **A159**, 172 (1932).

[67] Bikerman: Kolloid-Z., **42**, 293 (1927); Janek and Jirgensons: **41**, 40 (1927).

[68] Weiser: J. Phys. Chem., **28**, 1254 (1924); *cf., also,* Janek and Jirgensons· Kolloid-Z., **41**, 40 (1927).

[69] Weiser and Mack: J. Phys. Chem., **34**, 101 (1930).

ions by the dispersed particles. All these factors are measurable and are known to have more or less influence on the stability. Chaudhury [70] believes that the change in interfacial tension between the dispersed particles and the surrounding medium will have an important bearing on the tendency of the particles to coalesce. Although this may be true, it appears inadvisable to attach too much importance to a factor that cannot be measured, until it has been demonstrated that the above-mentioned measurable factors are inadequate to explain the observed facts.

Keeser [71] found that salts of cholesterol and lecithin sensitize arsenic trisulfide sols toward electrolytes. The activity of the sols of cholesterol esters in cutting down the stability of negative sols is reduced as the length of the carbon chain in the homologous series is decreased. The sensitizing action of the potassium and sodium salts of cholesterol sulfuric acid depends on the solubility of the salt. The constant ratio in the organism between free cholesterol and its esters may have an important bearing on the physical state of the body colloids. If poisons are removed from the body by combining with free cholesterol, such as happens in the removal of saponin, the normal physical condition of the cell colloids could be disturbed in the event that the resulting product has the properties of a cholesterol ester. This point of view may serve to account for the fact that an increase in the amount of cholesterol in the organism is always followed by an increase in the fatty acid phosphatides.

Kinetics of the Electrolyte Coagulation

The velocity of the slow coagulation of arsenic trisulfide sol has been followed by means of both a spectrophotometer and an opacity meter.[72] Using the former technique Mukherjee and Majumdar [73] found that Smoluchowski's theory (Vol. I, p. 89) applies only in the initial coagulation process, a limiting stage of coalescence being ultimately reached where the equations fail completely. This stage was reached more rapidly with lower concentrations, when the coagulation rate was slower. The results were explained by assuming, as Freundlich [74] does, that the coalescence is reversible or irreversible according to the magnitude of the ζ-potential of the particles. At sufficiently low

[70] J. Phys. Chem., **32**, 1485 (1928).
[71] Biochem. Z., **154**, 321 (1924); **157**, 166 (1925).
[72] Dumanskii and Shershnev: J. Russ. Phys.-Chem. Soc., **62**, 187 (1930).
[73] J. Chem. Soc., **125**, 785 (1924).
[74] Kolloid-Z., **23**, 163 (1918); *cf.* Kruyt and van Arkel: **32**, 29 (1923).

concentrations of electrolyte it is reversible, but is irreversible at higher concentrations when the ζ-potential is small. The limiting stage results when there is an equilibrium between the rates of breaking up of the aggregates and of coalescence. From similar experiments on arsenic trisulfide sol, using potassium chloride as precipitating electrolyte, Jablczynski [75] first obtained results for slow coagulation in good agreement with Smoluchowski's theory, provided the sol was not freed from hydrogen sulfide; but later [76] he found that the Smoluchowski equation had to be modified in order to make it applicable.[77]

The rate of coagulation of arsenic trisulfide sol is decreased by both visible and ultraviolet light; but the velocity is speeded up if a fluorescent substance like fluoresceine or eosin [78] is added to the sol before exposure to light. The effect is due to the fluorescence of the added dye since other colored compounds which do not fluoresce are without influence.

For every sol there appears to be a critical temperature above which it will coagulate (Vol. I, p. 190). The addition of increasing amounts of electrolytes not only lowers the critical temperature of stability but also greatly increases the velocity of coagulation at high temperatures.[79]

Mechanism of the Coagulation Process

Adsorption of Cations. The adsorption of cations by the arsenic trisulfide particles during the coagulation of sol was first reported by Linder and Picton.[80] Later Whitney and Ober [81] investigated the phenomenon and claimed that equivalent amounts of various cations were adsorbed by the same sol. This work was extended by Freundlich,[82] who at first observed an equivalent adsorption of ions of varying valence even when different sols were employed. Freundlich and coworkers [83] found a similar relationship with hydrous oxide sols

[75] Bull soc chim., (4) **35**, 1277 (1924).

[76] Jablczynski: Kolloid-Z., **54**, 164 (1931).

[77] *Cf., also,* Joshi and Prabhu. J. Indian Chem. Soc., **8**, 337 (1931).

[78] Boutaric and Bouchard: Compt. rend, **192**, 95 (1931); Bull. soc. chim., (4) **51**, 757 (1932); *cf.* Pospelov and Pospelova: J. Phys. Chem. (U.S.S.R.), **5**, 52 (1934)

[79] Burton, Deacon, and Annetts: Trans. Roy. Can. Inst., (4) **18**, pt. 1, 33 (1931).

[80] J. Chem. Soc., **67**, 64 (1895).

[81] Whitney and Ober: J. Am. Chem. Soc., **23**, 842 (1901).

[82] Kolloid-Z, **1**, 321 (1907); Z. physik. Chem., **73**, 408 (1910).

[83] Freundlich and Ishizaka: Kolloid-Z., **12**, 232 (1913); Gann: Kolloid-Beihefte, **8**, 73 (1916).

which led Freundlich to conclude that, in general, equivalent amounts of varying precipitating ions are adsorbed at the precipitation value with both positive and negative sols. This was not confirmed by the author with hydrous oxide sols [84] even for ions of the same valence; and, with arsenic trisulfide sols,[85] the adsorption values for the alkaline-earth cations were found to be similar but not identical for the same sol and to vary widely with different sols. Freundlich reached the same conclusion as the result of his most recent investigations.[86] The adsorption values obtained by the various investigators are collected in Table XXV. Although the tabulated results show considerable varia-

TABLE XXV

ADSORPTION OF CATIONS DURING THE PRECIPITATION OF ARSENIC TRISULFIDE SOL

Cation	Conc. of sol g/l	Adsorption m.eq./g	Observer	Cation	Conc. of sol g/l	Adsorption m.eq./g	Observer
Ba ..	6 4	0 116	Weiser *	Aniline.....		0.074	Freundlich §
Sr....	6 4	0 107	"	New fuchsin	..	0 076	"
Ca	6 4	0 093	"	UO_2	4 14	0 088	"
Ba	11 8	0 060	"	Ce . .	4 14	0 069	"
Sr.	11 8	0 056	"	Ba .	1.55	0 21	Freundlich ‖
Ca	11 8	0 043	"	Zn .	1 55	1 50	"
Ba .	21 5	0 072	"	Ni	1 55	1 22	"
Sr	21 5	0 069	"	In.. . .	. .	0 56	"
Ca .	21 5	0 073	"	Te . ..	.	0 37	"
Ba	10 0	0 110	Whitney and Ober †	Th .	.	0 27	"
				New fuchsin	.	0.08	"
Sr	10 0	0 082	"	Methylene blue		0 13	"
Ba ..	10.0	0 100	"				
Ba	3 33	0 086	Linder and Picton ‡				

* J. Phys. Chem., 29, 955 (1925).
† J. Am. Chem. Soc., 23, 842 (1901).
‡ J. Chem. Soc., 67, 64 (1895).
§ Kolloid-Z., 1, 321 (1907); Z. physik. Chem., 73, 408 (1910).
‖ Freundlich, Joachimsohn, and Ettisch: Z. physik. Chem., A141, 249 (1929)

tion from equivalent adsorption, it should be pointed out that the maximum variation does not exceed 20% until one reaches the most

[84] Weiser and Middleton: J. Phys. Chem., **24**, 53, 648 (1920).
[85] Weiser: J. Phys. Chem., **29**, 955 (1925).
[86] Freundlich, Joachimsohn, and Ettisch: Z. physik. Chem., **A141**, 249 (1929).

recent data reported by Freundlich. Unfortunately these data are probably the least accurate. Since Freundlich worked with a dilute sol and used potentiometric methods where such methods have not been accepted, it is probable that the results for the adsorption of zinc, nickel, and indium are inaccurate and should have been omitted from the table as were the values for sodium and hydrogen.

There are two main reasons why the adsorption values are not equivalent at the precipitation value: (1) even if the adsorption of equivalent amounts lowers the potential to the critical value, adsorption by the agglomerating particles takes place in varying amounts depending on the nature and concentration of the electrolyte; (2) less of a strongly adsorbed ion needs to be adsorbed in order to reduce the potential to the critical value.[87]

Neglecting the effect of the stabilizing ions of electrolytes, the precipitating ions which are most readily adsorbed will precipitate in the lowest concentration. From this it follows that the greater precipitating power of ions of higher valence results from their relatively greater adsorbability. Moreover, among ions of the same valence, the one with the greatest adsorption capacity will effect precipitation in the lowest concentration. Finally, the variation among electrolytes with the same precipitating ion and different stabilizing ions is caused in part by differences in the adsorbability of the latter.

Let us consider an ideal case fulfilling the following requirements: (1) the amounts of precipitating ions which must be adsorbed to lower the ζ-potential to the critical point are equivalent and depend only on the number of charges they carry; and (2) the effect of the stabilizing ion is a logarithmic function of its concentration, that is, follows the usual adsorption isotherm. Now if the amounts adsorbed in mols of the several ions which are proportional to the reciprocal of the valence are plotted against the precipitation concentration in millimols per liter, a curve is obtained like that shown in Fig. 33.

As is well known, a much higher molar concentration of a univalent ion is necessary to effect coagulation than of a multivalent ion. It is unnecessary to assume with Freundlich that the equivalent amounts are adsorbed from equimolar solutions. The isotherm of Fig. 33 is the curve of equivalent adsorption necessary for decreasing the potential to the critical value and must not be confused with the total amount that may be adsorbed on coagulation.

One might expect to approach most nearly the ideal conditions

[87] Weiser: J. Phys. Chem., **35**, 1, 1368 (1931); Weiser and Gray: **36**, 2178 (1932).

referred to in the preceding paragraph by working with strongly ionized salts having a common stabilizing ion and precipitating ions varying in valence but so similar chemically that the adsorption in mols will be proportional to the reciprocal of the valence. The common stabilizing ion will influence the adsorption of the precipitating ion

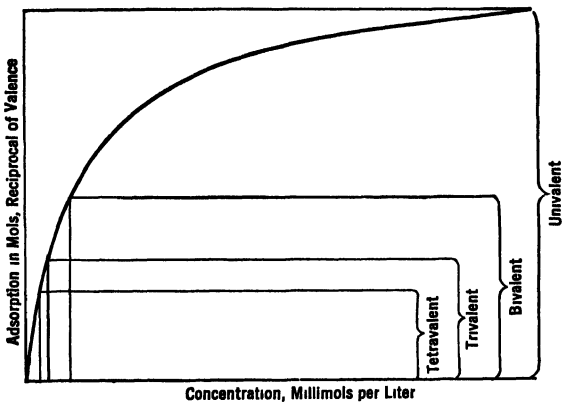


FIG 33.—Adsorption isotherm for cations of varying valence (diagrammatic).

logarithmically in proportion to the concentration. Such conditions are actually realized approximately in the precipitation of arsenic trisulfide sol by cobalt amines with cations varying in valence from 1 to 6. The average precipitation values for a series of such salts as observed by Matsuno [88] are given in Table XXVI. In these experiments a rela-

TABLE XXVI

PRECIPITATION VALUES OF COBALT AMINES FOR ARSENIC TRISULFIDE SOL

Valence of cation	No. of salts examined	Precipitation values (average) millimols/l	
		Observed	Calculated
1	7	5330 0	5130 0
2	5	360 0	333 0
3	6	66 6	66 6
4	4	18 8	22 0
6	1	4 2	4 3

[88] J. Coll. Sci. Imp. Univ. Tokyo, **41**, *M*11, 1 (1921).

tively small amount of sol was coagulated by an excess of cobalt salt so that the amount adsorbed may be neglected in comparison with the precipitation value. In Fig. 34 the precipitation values are plotted against the reciprocal of the valence, giving an isotherm similar to the diagrammatic one. In the same figure are plotted also the logarithms of the precipitation values against the logarithms of the reciprocal of the valence. An approximately straight line is ob-

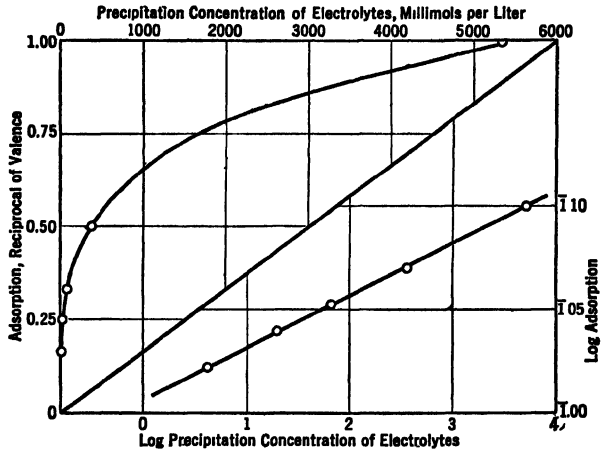


FIG. 34.—Relationship between the valence of cobalt amine cations and the precipitation concentrations for arsenic trisulfide sol.

tained, from the slope of which one may calculate the precipitation values and compare with the observed values [89] (see Table XXVI). Freundlich and Zeh [90] confirmed the observations of Matsuno, by a study of the effect of the various cobalt amines on the cataphoretic mobility of arsenic trisulfide. Similar observations on hydrous ferric oxide in the presence of complex cyanide ions of varying valence revealed as usual a specific adsorption factor in addition to valence. Thus the precipitating power of $Au(CN)_4^-$ appears to be twelve times as great as $Au(CN)_2^-$ and that of $Fe(CN)_6^{---}$ only twice as great as $Pt(CN)_4^{--}$.

If the adsorption theory as outlined by Freundlich were generally applicable then, as Ostwald [91] points out, the following relationship be-

[89] *Cf* Freundlich: Kolloid-Z., **31**, 243 (1922).
[90] Z. physik. Chem., **114**, 65 (1924).
[91] Kolloid-Z., **26**, 28, 69 (1920).

tween the valence and the precipitating power of an ion should hold:

$$\frac{1}{C_1} : \frac{1}{C_2} : \frac{1}{C_3} \cdots = 1 : 2^n : 3^n \cdots$$

where C_1, C_2, and C_3 are the precipitation values of electrolytes with univalent, bivalent, and trivalent precipitating ions and n is a constant. This recalls the older formula of Whetham:[92]

$$\frac{1}{C_1} : \frac{1}{C_2} : \frac{1}{C_3} \cdots = 1 : x : x^2 \cdots$$

where the C's have the same significance as above and x is a constant. Formulas of this kind fit the experimental data so roughly that they are of questionable use (p. 192).

Titration of Sols. Whitney and Ober[81] observed that barium, but not chloride is adsorbed during the precipitation of arsenic trisulfide sol with barium chloride and that hydrochloric acid equivalent to the adsorbed barium is present in the supernatant solution. This was believed to be a case of hydrolytic adsorption, but Rabinovich[93] showed it to be an exchange adsorption in which hydrogen ions in the outer portion of the double layer are exchanged for barium ions. The hydrogen ion concentration of the sol may be determined conductometrically,[94] but the method is of doubtful accuracy especially in sol-electrolyte mixtures. Weiser and Gray[95] adopted the more satisfactory procedure of potentiometric analysis with the glass electrode. Determination of the change in hydrogen ion concentration on the stepwise addition of coagulating electrolyte has been called "titration of sol." The method was as follows: To 10-cc portions of sol containing 10 g As_2S_3/l were added, in a mixing apparatus, definite amounts of electrolytes diluted to 5 cc. The pH value of each sol was first determined, after which the pH of the water and electrolyte were brought to this value with hydrochloric acid; thus, the observed displacements of hydrogen ion were real and not due to dilution effects. A typical set of data using barium chloride is given in Table XXVII and presented

[92] Phil. Mag., (5) **48**, 474 (1899); *cf.* Robertson: "Die physikalische Chemie der Proteine," Dresden, 94 (1911).

[93] Z. physik. Chem., **116**, 97 (1925).

[94] Pauli and Semler: Kolloid-Z., **34**, 145 (1924); Rabinovich: Z. physik. Chem., **116**, 97 (1925); Rabinovich and Dorfmann: **131**, 313 (1928).

[95] J. Phys. Chem., **36**, 2796 (1932).

graphically in Fig. 35 together with the titration curves for the chlorides of strontium, calcium, and aluminum. The coagulation point for each electrolyte is indicated by an arrow.

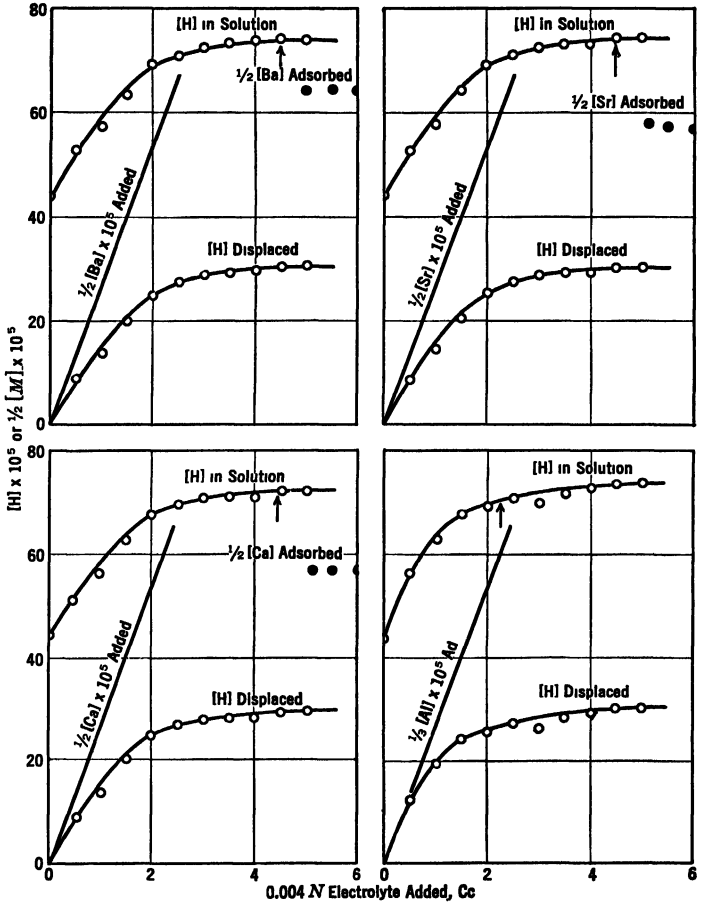


FIG. 35.—Titration curves of arsenic trisulfide sol with various electrolytes.

The adsorption values for the cations above the precipitation value were determined on 100-cc portions of sol to which were added definite amounts of electrolyte diluted to 50 cc, thus giving data comparable to the titration data.

TABLE XXVII

TITRATION OF ARSENIC TRISULFIDE SOL WITH BARIUM CHLORIDE

0 004 *N* $BaCl_2$ added cc	$[H^+] \times 10^6$ in solution	$[H^+] \times 10^6$ displaced	Electrolyte added equivalents $\times 10^6$
0 0	43 7	0 0	0 0
0 5	52 5	8 8	13 3
1 0	57 5	13 8	26 7
1 5	63 1	19 4	40 0
2 0	69 2	25 5	53 3
2 5	70 8	27 1	66 7
3 0	72 5	28 8	80 0
5 0	74 1	30 4	133 3

A set of curves showing the displacement of hydrogen ion by cations of varying valence is given in Fig. 36. The marked displacing action of aluminum ion, especially at low concentrations, is in line with the higher precipitating power of aluminum chloride, whereas the rela-

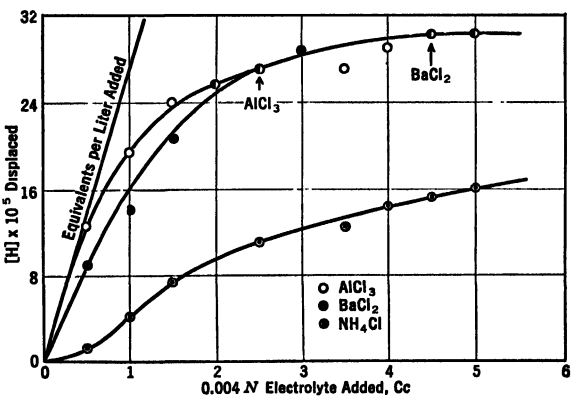


FIG 36.—Displacement of hydrogen ion from arsenic trisulfide particles by cations of varying valence.

tively weak displacing action of ammonium ion is in accord with the relatively low precipitating power of ammonium chloride. It will be noted that the ratio of the precipitation value, in millimols per liter, of barium chloride to aluminum chloride is 2.1 in the sol under consideration containing 10 g/l as compared with 7.4 in the sol containing but

1.8 g/l (Table XIX). This supports the rule that the precipitation value varies approximately as the concentration of the sol for trivalent ions and is almost independent of the concentration of the sol for bivalent ions. Obviously, precipitation rules which presume to give the ratio of the precipitating power of ions of varying valence (p. 207) must take into account the way in which the precipitation value is influenced by the concentration of sol.

The curves in Fig. 35 show that, in the sol under consideration, somewhat more than one-third of the total hydrogen ion in solution after coagulation was displaced from the particles, the remainder being measurable potentiometrically in the original sol. The adsorption of the several cations was approximately twice as great as the hydrogen displaced from the diffuse outer layer, meaning that a portion of the adsorbed cation corresponds to hydrogen ion in the outer layer that is measurable in the original sol. The adsorption was from 14 to 22% less than the total hydrogen ion in solution after coagulation. It was a fortuitous combination of circumstances that gave Whitney and Ober a filtrate having the same amount of hydrogen ions as the amount of barium adsorbed.

Rabinovich [96] concluded from conductometric measurements that equivalent amounts of barium, say, are adsorbed and hydrogen ion displaced in the first stage of the coagulation process, which is followed by a second stage, the agglomeration of the particles. It is probable that the observed equivalence between adsorption and hydrogen ion displacement results from the limitations in his experimental method. In any event only the part of the counter ions in the diffuse outer layer which are not measurable in the original sol can be displaced. What Rabinovich doubtless means is that barium goes into the outer layer in exchange for an equivalent amount of hydrogen; but this could be determined definitely only by measuring the pH of the sol and of the ultrafiltrate from the sol after the addition of electrolyte, as Verwey and Kruyt did with silver iodide sol (p. 120). Rabinovich is concerned because precipitation does not follow immediately after the completion of the exchange adsorption. As a matter of fact, depending on the conditions the coagulation may take place before, after, or at the point where the displacement of hydrogen ion is complete. It is a question not of the amount of hydrogen displaced from the innermost portion of the outer layer but of sufficient contraction of the double

[96] Rabinovich and Wasseliev: Kolloid-Z., **60**, 268 (1932); Rabinovich and Fodimann: Z. physik. Chem., **A154**, 255 (1931); Rabinovich and Kargin: **A143**, 21 (1929).

layer as a result of adsorption of the added cation to lower the potential on the particles to the critical value. Referring to Fig. 36 it will be seen that the precipitation concentration for barium chloride is above the value necessary for displacing all the hydrogen, whereas, with aluminum chloride, coagulation takes place a little before all the hydrogen is displaced. With the hydrous oxide sols the author found repeatedly (Vol. II, pp. 73, 114, 142) that coagulation occurred before all the counter chloride ions in the innermost portion of the outer layer were displaced by precipitating anions. Moreover, fewer chloride ions were displaced at the precipitation value of a trivalent anion than of a bivalent one. All of which means that the displacement of the counter ions by the precipitating ion is of secondary importance. As a rule, most of the counter ions will be displaced before the adsorption of the precipitating ions is sufficient to lower the potential to the critical value. It would be altogether surprising, however, if the adsorption were always sufficient at the point where the displacement was complete. The fact that it is not with barium chloride as precipitant for arsenic trisulfide sol led Rabinovich to postulate the existence of two phases in the coagulation. The author has no objection to considering potential lowering and agglomeration as two separate phases of the coagulation process, but not for the reasons advanced by Rabinovich.

The order in which the several chlorides displace hydrogen ion from the arsenic trisulfide particles is: $Al > Ba$, $Sr > Ca > NH_4$. This is likewise the order of precipitating power of the several electrolytes and the order of adsorption of the several cations at concentrations below the precipitation value.

To account for the observed behavior, the constitution of the hydrous sol may be represented diagrammatically as shown in Fig 37*A*, S^{--} and HS^{-} being the potential-determining ions which constitute the inner portion of the double layer with hydrogen ions in the diffuse outer portion. The hydrogen ions not measurable potentiometrically in the original sol are represented between the particle and the dotted line.

On adding an electrolyte such as barium chloride to the sol the strongly adsorbed barium ions enter the outer layer, displace hydrogen ions, and take up a position relatively closer to the inner layer than hydrogen ions, as shown diagrammatically in Fig. 37*B*. This contraction of the double layer, and increase in charge density of the outer layer, result in a lowering of the potential on the particles to the point where collisions result in partial coalescence and agglomeration. Because of the stronger adsorption of the aluminum ions, the thickness

of the double layer is less than with bivalent barium ions. Accordingly, less aluminum needs to be adsorbed to reduce the potential to the coagulation point, and precipitation takes place with lower concentrations of aluminum salts than of barium salts. With the weakly adsorbed ions such as ammonium, a relatively high concentration is necessary to increase the charge density in the outer layer and so lower the potential to the coagulation point. Because of the weaker adsorp-

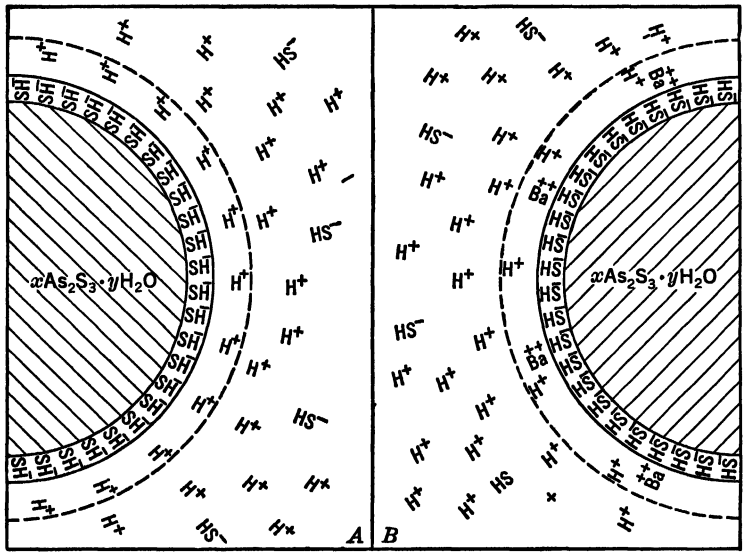


FIG. 37.—Diagrammatic representation of the constitution of a particle in an arsenic trisulfide sol (*A*) before and (*B*) after the addition of barium chloride.

tion of ammonium than of aluminum and barium, the displacement of hydrogen by ammonium from the portion of the outer layer represented within the dotted line is much less than with an equivalent amount of the multivalent ions.

As already pointed out, the adsorption of multivalent cations at their precipitation value is much greater than the hydrogen displaced. The reason is obvious, since a part of the adsorbed ion takes the place of hydrogen in the outermost portion of the diffuse layer.

The mobility of ammonium ion is retarded in the presence of arsenic trisulfide. The observed effects were attributed to exchange adsorption and the action of the diffuse double layer.[97]

[97] Bikerman: Trans. Faraday Soc., **33**, 560 (1937).

Mutual Action of Sols

Hydrophobic Sols

When suitable amounts of two sols of opposite sign are mixed, complete mutual coagulation takes place. This is ordinarily attributed to the mutual discharge of the electrically charged particles of opposite sign with subsequent agglomeration into clumps that settle out. The observations of Biltz [98] are commonly cited to show that the action is determined only by the amount of the charge on the particles and not at all by their nature.[99] Thus a comparison of the precipitating action of a series of sols is said to disclose that, whereas the optimum amount of positive sols required to precipitate negative sols varies,

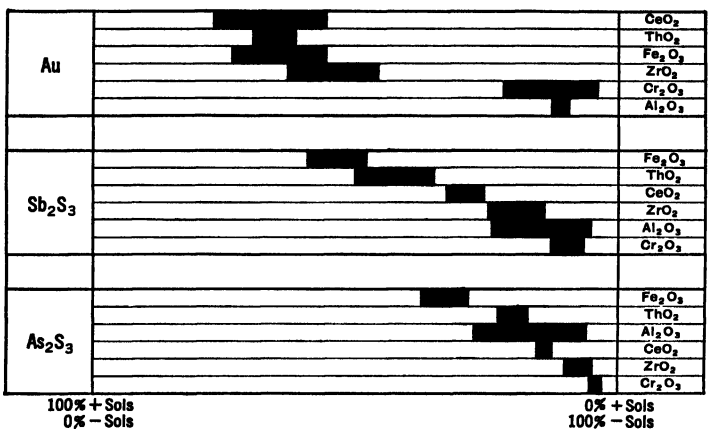


Fig 38.—Range of mutual coagulation of oppositely charged sols (Biltz).

the order is always the same. That this is not true is evident from Biltz's results when given in the form of a diagram as in Fig. 38.[100] The zone of complete mutual coagulation is shown in black. The positively charged hydrous oxide sols are arranged in the order of their precipitating power for the three negative sols; obviously the orders are not the same. Similar experiments with three hydrous oxide sols and a series of negative sols including arsenic trisulfide were carried out

[98] Ber., **37**, 1095 (1904).

[99] Freundlich: "Kapillarchemie," 402 (1909); Thomas: Bogue's "Colloidal Behavior," **1**, 325 (1924).

[100] Weiser and Chapman: J. Phys. Chem, **35**, 543 (1931); Bancroft: **19**, 363 (1915); *cf.* Joshi and Pannikkar: J. Indian Chem. Soc., **11**, 797 (1934).

by Weiser and Chapman, taking special precautions to determine sharply the zone of mutual coagulation. The results represented diagrammatically in Fig. 39 show a wide variation in the order of precipitating power of the negative sols for the three positive sols. Wintgen and Löwenthal [101] state the generally accepted view in another way when they say that the mutual precipitation of oppositely charged sols is a maximum when the concentrations of the sols expressed in equivalent aggregates are the same, that is, when equal numbers of charges of opposite sign are mixed. This rule was likewise found

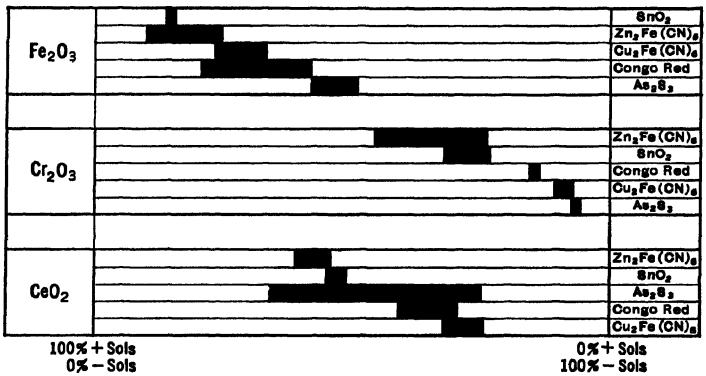


FIG 39.—Range of mutual coagulation of oppositely charged sols.

not to hold when a highly dispersed sol of one sign is mixed with a coarser sol of opposite sign.

Lottermoser [102] observed that the most nearly complete coagulation of positively charged silver iodide containing a slight excess of silver nitrate, and negatively charged silver iodide containing a slight excess of potassium iodide, was obtained when the excess of silver nitrate in one sol was just equivalent to the excess of potassium iodide in the other. This suggests that interaction between the stabilizing ions is the cause of the mutual coagulation of oppositely charged sols. In line with this, Freundlich and Nathansohn [103] found colloidal arsenic trisulfide sol and Odén's sulfur sol to be instable in the presence of

[101] Z. physik. Chem., **109**, 391 (1924); *cf.* Lottermoser and May: Kolloid-Z, **58**, 61 (1932).

[102] Kolloid-Z., **6**, 78 (1910).

[103] Kolloid-Z., **28**, 258 (1920); **29**, 16 (1921); *cf.* Chernstitskaya and Kargin: J. Phys. Chem (U.S.S.R.), **9**, 461, 471, 481 (1937).

each other. Since both sols are negatively charged, this instability cannot be due to mutual electrical neutralization but was found to result from interaction between the stabilizing electrolytes of the two sols, hydrogen sulfide and pentathionic acid. Following up the above suggestion, Thomas and Johnson [104] attribute mutual coagulation in other cases primarily to chemical interaction of the stabilizing electrolytes in the sols. This cannot be generally true since mutual coagulation takes place very frequently where interaction between stabilizing agents is a remote possibility.[105] For the behavior of colloidal silver and arsenic trisulfide in contact with each other see Vol. I, pp. 131-132.

Boutaric and Dupin [106] followed the course of the mutual coagulation of ferric oxide and arsenic trisulfide sols by measuring the rate of increase in opacity with a spectrophotometer. As would be expected, a certain amount x of one must be added before any coagulation takes place, above which the velocity increases until it becomes instantaneous, then falls off again, and finally, when more than the quantity y is added, there is no further coagulation. Decreasing the particle size, or increasing the proportion of hydrogen sulfide in the arsenic trisulfide sol, does not affect x for ferric oxide sol but it increases y. The longer the ferric oxide sol is dialyzed the lower the y-value for arsenic trisulfide, but x is not altered much. The values of x and y are consistent whether one adds arsenic trisulfide sol to ferric oxide sol or the reverse. These observations of the effect of varying purity of sol on the zone of mutual coagulation have been confirmed and extended by Weiser and Chapman. To account for the behavior of various combinations it was concluded [107] that the precipitating power of positive sols for negative sols is not determined exclusively by the magnitude of the ζ-potential of the particles in the respective sols. Other factors that may come in are: (a) mutual adsorption of oppositely charged particles that may be independent of their potential resulting from adsorbed ions, (b) the presence of precipitating ions as impurities in the sols, and (c) the interaction between stabilizing ions.

From the mobility measurements on mixtures of positively and negatively charged sols with and without the addition of electrolytes,

[104] J. Am. Chem. Soc., **45**, 2532 (1923).

[105] *See 10 examples in* Weiser and Chapman: J. Phys. Chem., **35**, 543 (1931).

[106] Bull. soc. chim., **43**, 44, 1059 (1928).

[107] Weiser and Chapman: J. Phys. Chem., **35**, 543 (1931); **36**, 713 (1932); *cf.* Bahl: Kolloid-Z., **59**, 60 (1932).

Hazel and McQueen [108] conclude that mutual coagulation is due primarily to mutual adsorption of oppositely charged particles with a consequent unequal redistribution of the total charges around the particles.

Hydrophilic Sols

Although gelatin is usually regarded as a protecting colloid for sols, cutting down the precipitating action of electrolytes, Billitzer [109] showed that sols of the sulfides of arsenic and antimony are precipitated by small amounts of gelatin. In larger amounts, it adsorbs the arsenic trisulfide, converting the whole into a stable positive sol. The sensitization of arsenic trisulfide sols toward electrolytes by the addition of small amounts of gelatin has been observed repeatedly.[110, 111] Peskov [112] claims, however, that highly purified gelatin sols are unable to cause coagulation of other sols unless the former are concentrated and contain large particles. Negatively charged gelatin in small concentrations may precipitate negative arsenic trisulfide probably by adsorbing the peptizing ion and thus reducing the potential.[113] Sugden and Williams [111] claim that gelatin sensitizes arsenic trisulfide sol at low concentrations and even coagulates it without more than traces of electrolyte being present. Müller and Artmann [114] report that gum and casein are better protecting colloids for arsenic trisulfide sol than are glue and isinglass. Sodium and potassium soaps protect the sol in the following order: linoleate > oleate > palmitate > stearate > myristate > laurate.[115]

Ion Antagonism in the Coagulation of Sols

Linder and Picton,[116] in their early work on the coagulation of sols by electrolytes, observed that the precipitating action of mixtures of two electrolytes for arsenic trisulfide sol is approximately additive provided the precipitating power of each is of the same order of

[108] J. Phys. Chem., **37**, 553, 571 (1933).

[109] Z. physik. Chem., **51**, 145 (1905).

[110] Boutaric and Perreau: Compt. rend, **181**, 511 (1925); Ghosh and Dhar: Kolloid-Z., **41**, 229 (1927).

[111] Sugden and Williams: J. Chem. Soc., 2424 (1926).

[112] J. Russ. Phys.-Chem. Soc., **49**, 1 (1917).

[113] Peskov and Sokolov: J. Russ. Phys.-Chem. Soc, **58**, 823 (1926).

[114] Chem. Zentr., I, 1388 (1904).

[115] Papaconstantinou: J. Phys. Chem., **29**, 319 (1925); *cf.* Bhatnagar, Prasad, and Bahl: J. Indian Chem. Soc., **2**, 11 (1925).

[116] J. Chem. Soc., **67**, 67 (1895).

magnitude, whereas the precipitating action may rise appreciably above an additive relationship if the electrolytes vary widely in their precipitating power. For example, the precipitating action of mixtures of strontium chloride and barium chloride are nearly additive, whereas the addition of potassium chloride increases rather than decreases the precipitation concentration of strontium chloride. This cannot be attributed to a decrease in the dissociation of strontium chloride by potassium chloride because other potassium salts, such as the nitrate, give similar results. Since the so-called ion antagonism was not observed with gold sol or with von Weimarn's sulfur sol, but was observed with Odén's sulfur sol which is hydrous, Freundlich and Scholz [117] conclude that the hydration of the sol and of the precipitating ion are of primary importance in producing ion antagonism and so in determining whether the precipitating action of mixtures shall be additive or above the additive value (Vol. I, p. 323). This leads to the deduction that arsenic trisulfide sol is a hydrophile sol although it is not usually so considered; and to the suggestion that the behavior of colloids with mixtures is a suitable means of determining to what extent the stability is influenced by hydration. The general accuracy of these conclusions is rendered questionable by some observations on the precipitation of chromic oxide sol [118] by mixtures of electrolytes having widely different precipitating power, such as potassium chloride and potassium sulfate. Although this sol is highly hydrous, the precipitation values of mixtures are somewhat less than additive instead of being considerably above the additive values as the theory of Freundlich and Scholz would predict. One may be quite certain, therefore, that hydration is not the only factor in bringing about the phenomenon of ion antagonism and may be a relatively unimportant one in certain cases.

As a result of an investigation of this anomalous behavior, in 1921,[119] it was concluded that, in the simultaneous adsorption by solids from mixtures of two electrolytes having no ion in common, the most readily adsorbed cation and anion are taken up most and the other pair least readily; whereas, from mixtures having one ion in common, the oppositely charged ions are each adsorbed less than if the other were absent, but the most readily adsorbed ion is displaced the least. This is illustrated in Table XXVIII,[85] which gives the pre-

[117] Kolloid-Beihefte, **16**, 267 (1922); *cf., also,* Neuschlosz: Pfluger's Arch., **181**, 17 (1920); Dorfmann: Kolloid-Z., **46**, 186 (1928); **52**, 66 (1930).

[118] Weiser: J. Phys. Chem, **28**, 232 (1924).

[119] Weiser: J. Phys. Chem., **25**, 665 (1921).

cipitation values of barium chloride and the alkali chlorides for arsenic trisulfide sol together with the adsorption of barium ion during the precipitation of the sol with barium chloride alone and when mixed with a constant amount of the several alkali chlorides. It is apparent that univalent ions cut down the adsorption of barium in the order: Li < Na < K < H. Since under otherwise constant conditions, one

TABLE XXVIII

ADSORPTION OF BARIUM ION BY ARSENIC TRISULFIDE

Electrolytes added to 100 cc sol Total volume 200 cc	Barium adsorbed m.eq./g	Precipitation values millimols/l	
30 cc 0 02 *N* $BaCl_2$	0 058	$BaCl_2$	1 37
30 cc 0 02 *N* $BaCl_2$ + 30 cc 0 5 *N* LiCl .	0 019	LiCl	88 7
30 cc 0 02 *N* $BaCl_2$ + 30 cc 0 5 *N* NaCl	0 014	NaCl	73 5
30 cc 0 02 *N* $BaCl_2$ + 30 cc 0 5 *N* KCl.	0 009	KCl	63 7
30 cc 0 02 *N* $BaCl_2$ + 30 cc 0 5 *N* HCl .	0 007	HCl	52 5

would expect the adsorption of a given cation to be cut down by the presence of a second cation in proportion to the adsorbability of the latter, it follows that the order of adsorbability of the univalent ions is: H > K > Na > Li. This is exactly the same as the order one would deduce from the precipitation values of the salts (Table XXVIII) assuming that the salt containing the most readily adsorbed cation precipitates in lowest concentration.

It should be pointed out in passing that the results recorded in Table XXVIII furnish almost conclusive proof that univalent cations are adsorbed less strongly [120] than bivalent barium.

Since there would appear to be a mutual cutting down of the adsorption of ions of like charge when sols are coagulated by mixtures, two factors in addition to hydration may influence the precipitating action of mixtures · [119] (1) the antagonistic effect of each precipitating ion on the adsorption of the other, and (2) the stabilizing influence of the ions having the same charge as the sol.

To illustrate the antagonistic action, some observations with mix-

[120] *Cf., however,* Dhar, Sen, and Ghosh: J. Phys. Chem., **28**, 457 (1924); Freundlich, Joachimsohn, and Ettisch: Z. physik. Chem., **A141**, 249 (1929).

tures of lithium and barium chloride are given in Table XXIX.[121] Since it makes a difference whether the salts are added simultaneously or separately with an intervening time interval,[122] the former procedure was used. In the precipitation experiments, 10 cc of the sol containing 22.3 g As_2S_3/l were mixed with the volume of electrolytes indicated in the table, in a total volume of 5 cc. For the sake of accuracy, the adsorption experiments were carried out with 12.5 times the amounts of electrolyte and sol that were used in finding the pre-

TABLE XXIX

PRECIPITATION OF As_2S_3 SOL WITH MIXTURES OF $BaCl_2$ AND LiCl AND THE ADSORPTION OF Ba^{++} ION

0 5 *N* LiCl taken cc	0 01 *N* $BaCl_2$ to complete coagulation			Adsorption of Ba^{++} ion g/mol As_2S_3
	Taken cc	Calculated cc	Difference %	
4 05	.	..	...	. .
	4 03		.	
0 00	4.50		.	1 310
0 50	4 50	3 54	27	0 971
0 00	4 25		. .	1 250
1 00	4 25	3 03	38	0 841
0 00	3 76			1 145
2 00	3 76	2 03	84	0.520
3 00	2 25	1 03	118	

cipitation values. The adsorption data are the average of two or more determinations in each case.

The above results show the marked influence of lithium ion on the adsorption of barium ion. Thus, at the precipitation concentration of a mixture containing but one-eighth the precipitation value of lithium chloride alone, the adsorption of barium ion is lowered more than 25%, whereas from a mixture containing one-half the precipitation value of lithium chloride alone the adsorption of barium ion is decreased more than 50%. At the same time the presence of barium ion unquestionably influences the adsorption of lithium ion. This

[121] Weiser: J. Phys. Chem., **28**, 232 (1924); **30**, 20 (1926); *cf., also,* Boutaric and Perreau: Compt. rend, **180**, 1337; Boutaric and Manière: 1841 (1925); Dumanskii and Vinnikova: J. Phys. Chem. (U.S.S.R.), **5**, 133 (1934).

[122] Freundlich and Tamchyna: Kolloid-Z., **53**, 288; Buzágh, Freundlich, and Tamchyna: 294 (1930).

mutual action must have some effect in raising the precipitation values of certain mixtures above the additive value.

Since alkali cations cut down the adsorption of barium ion in varying degrees, one would expect the precipitation value of barium chloride to vary with the nature of the alkali ion. That such is the case is shown graphically in Fig. 40, in which the concentration of barium chloride is plotted against that of the univalent chloride at the precipitation value of the mixture. In the same figure, the precipitation concentrations of mixtures of potassium and sodium chloride are

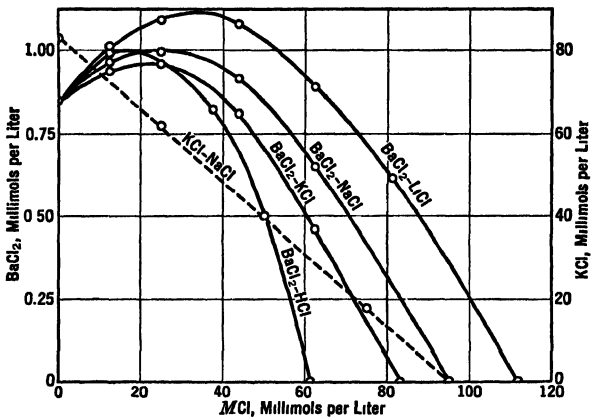


FIG 40.—Coagulation of arsenic trisulfide by mixtures of electrolytes

given to show the additive relationship which obtains with mixtures of similar precipitating power.

Associated with the cation antagonism is the effect of the chloride ion which cannot be ignored at the relatively high concentrations of alkali chloride employed. The similarity in form of the curves in Fig. 40 to that of the mobility curves frequently obtained on adding alkali halides to negative sols (p. 182) suggests a common explanation.[123] In most cases Dhar [124] and his collaborators rule out the in-

[123] *Cf.* Moyer and Bull: J. Gen. Physiol., **19**, 239 (1935); Bull and Gortner: J. Phys. Chem., **35**, 700 (1931); Vester: "Het Antagonisme der Electrolyten bij de Uctolokking van Sunspensoiden," Amsterdam (1935).

[124] J. Phys. Chem., **28**, 313, 457, 1029 (1924); **29**, 435, 517, 659 (1925); Kolloid-Z., **34**, 262 (1924); **36**, 129 (1925); Sen and Mehrotra: Z. anorg. Chem., **142**, 345 (1925); *see, also,* Mukherjee and Ghosh: J. Indian Chem Soc, **1**, 213 (1924); *cf., however,* Ghosh, Bhattacharya, and Dhar: Kolloid-Z., **38**, 145 (1926).

fluence of cation antagonism in increasing the precipitation value of certain salt pairs above the additive value, and attribute the effect entirely to the stabilizing action of anions. Certainly this effect predominates if one of the electrolytes contains a potential-determining ion, for example in the precipitation of negative copper ferrocyanide sol with mixtures of potassium ferrocyanide and barium chloride (p. 324). Freundlich has swung around to this point of view but he emphasizes also the importance of hydration of the particles as well as the hydration of the ions involved. Although the author was the first to point out the necessity of taking into account the effect of the ion having the same charge as the sol, he still believes that the antagonism between ions of the same sign, as recorded in Table XXIX, must be a contributing factor in certain cases. Ostwald [125] has shown recently that cation antagonism follows with certain salt pairs when the cation activity coefficients of the binary mixtures are substituted for concentrations.

The phenomena considered above have been observed chiefly with negative sols, but Freundlich [126] observed a similar behavior with arsenic trisulfide sol rendered positive by malachite green. For the results of observations with ferrocyanide sol see p. 322.

[125] Ostwald and Hoffmann Kolloid-Z, **80**, 186 (1937).
[126] Freundlich and Tamchyna. Kolloid-Z., **58**, 288 (1930).

CHAPTER XI

THE COLLOIDAL SULFIDES OF ANTIMONY, BISMUTH, TIN, AND LEAD

COLLOIDAL ANTIMONY TRISULFIDE

The Precipitated Salt

Antimony trisulfide occurs in nature as black orthorhombic crystals known as stibnite. The alchemist "Basil Valentine" prepared an amorphous red sulfide by subliming stibnite with ammonium chloride. In this way, antimony trichloride and ammonium sulfide were first formed and reacted on cooling to give the original compounds, the trisulfide separating as a red powder. Glauber and also Lenery speak of the solution of stibnite in caustic alkalis and the subsequent precipitation of a red powder but it was not until 1714 that particular attention was called to the preparation. In that year Simon, a Carthusian monk, was reported to have restored another monk to health by the administration of the powder prepared by a German apothecary, a disciple of Glauber. Simon gave to the powder the name *alkermes* or *kermes* mineral by which it is still known. The original method of formation consisted in boiling the crude sulfide with alkali until a clear solution was obtained from which the kermes separated. The preparation was at first believed to be a compound of antimony, sulfur, and alkali, but it is now known to be antimony trisulfide with more or less antimony trioxide and adsorbed alkali. The presence of impurities was objectionable for its use as a therapeutic agent, and so, in later modifications of the original process, the solution and subsequent precipitation of the sulfide were carried out in the absence of air and any trioxide was extracted with tartaric acid.

By passing hydrogen sulfide into a slightly acidified antimonous salt solution, the trisulfide is thrown down as a hydrous mass varying in color from golden yellow to orange-red, depending on the conditions of precipitation. When obtained from chloride solution it adsorbs chloride,[1] and the precipitate dried at 105° usually contains a

[1] Youtz: J. Am. Chem. Soc., **30**, 975 (1908).

small amount of sulfur, probably from the oxidation of adsorbed hydrogen sulfide. The precipitated compound adsorbs water quite strongly. Prolonged drying over sulfuric acid is reported to give a dihydrate, $Sb_2S_3 \cdot 2H_2O$,[2] but this composition is doubtless an accidental result of the conditions of drying. When dried at 100° it still retains adsorbed water which is given up gradually on heating to higher temperatures.[3] In order to remove all the water in the quantitative estimation of antimony as trisulfide,[4] it is necessary to heat the amorphous precipitate in a current of carbon dioxide until it goes over to the black crystalline form which adsorbs very little water.

If a dilute acid solution of antimony trichloride is treated with a solution of sodium thiosulfate, a bright red sulfide is obtained which has been called crimson sulfide, antimony cinnabar, and antimony vermilion. The color and composition depend on the method of formation, but it always consists of antimony trisulfide with more or less sulfur. The precipitation is quantitative in the presence of as low acid concentration as 0.17–1 *N* $HC_2H_3O_2$, whereas for quantitative precipitation of arsenic 8–10.5 *N* H_2SO_4 is required.[5] The various precipitated sulfides are said to be amorphous to x-rays;[6] but if heated to temperatures around 200° they are converted into black crystalline Sb_2S_3 having the same crystal structure as the mineral stibnite. The effect of method of preparation on the physical character and color of antimony trisulfide and the factors influencing the transformation to the definitely crystalline form will be considered in the chapter on the sulfide pigments (p. 299).

Antimony Trisulfide Sols

Formation. A very dilute yellow antimony trisulfide sol is obtained by passing hydrogen sulfide into a saturated solution of antimony trioxide in water. More concentrated sols are prepared by conducting hydrogen sulfide into a solution of potassium antimony tartrate or of the oxide dissolved in tartaric acid.[7] The maximum concentration of antimony salt that can be employed will give a sol containing approximately 5 g Sb_2S_3/l; if higher salt concentrations are used the

[2] Ditte Compt. rend., **102**, 212 (1886).
[3] De Bacho· Ann. chim. applicata, **12**, 143 (1919).
[4] Fresenius-Cohn: "Quantitative Chemical Analysis," **1**, 397 (1908).
[5] Kurtenacker and Fürstenau: Z. anorg. Chem., **215**, 257 (1933).
[6] Currie: J. Phys. Chem., **30**, 236 (1926).
[7] Schulze: J. prakt. Chem., (2) **27**, 320 (1883); *cf.* Heyer: Crell's "Chem. Ann," **2**, 227. 321, 493 (1785).

sulfide precipitates. The most satisfactory method of preparing the sol [8] consists in allowing 200 cc of a tartar emetic solution to drop slowly into a like volume of water saturated with hydrogen sulfide through which the gas is kept bubbling. The excess hydrogen sulfide may be removed by a current of hydrogen or by boiling. Boiling is not recommended, however, since the size of the particles is increased, the sulfide is hydrolyzed appreciably,[9] and the stability of the sol is reduced. The sols may be purified to a certain extent by dialysis, but if the process is continued too long all the sulfide separates out. Just as with arsenic trisulfide sol (p. 173), Pauli, Kölbl, and Laub [8] purified and highly concentrated antimony trisulfide sols by the process of electrodecantation.

To increase the stability of the sols so that they can be sterilized for therapeutic purposes, Wolvekamp [10] uses the sodium salts of protalbinic and lysalbinic acids as protecting colloids. Soap [11] is also adsorbed by antimony trisulfide and acts as a protecting colloid. Utzino [12] ground antimony trisulfide in a colloid mill with grape sugar, obtaining sols which appear to show a maximum stability not at the finest state of subdivision. Other conditions being the same, this result cannot be correct. The adsorption of such sugars as arabinose, maltose, and levulose at varying concentrations by antimony trisulfide sol has been followed [13] by means of the polarimeter, since adsorbed sugar does not affect the plane of polarized light. In certain instances the increase in adsorption with increasing concentration of sugar can be represented quite accurately by the Freundlich equation.

Properties. The color of antimony trisulfide sols varies widely with the dilution, as indicated in Table XXX. As with the corresponding arsenic sol, it makes a difference whether a dilute sol is prepared directly or whether a concentrated sol is diluted; the diluted sol always contains larger particles and so appears more cloudy in reflected light.[14] The absorption spectrum of the sol is a continuous band from the violet to the blue.[15]

Antimony trisulfide sol is negatively charged owing to adsorption

[8] Biltz: Ber., **37**, 1097 (1904); Pauli, Kölbl, and Laub: Kolloid-Z., **80**, 175 (1937).

[9] Elbers: Chem.-Ztg., **12**, 355 (1888).

[10] U S. Pat. 1,412,438 (1920).

[11] Bhatnagar, Prasad, and Bahl: J. Indian Chem. Soc., **2**, 11 (1925).

[12] Kolloid-Z., **32**, 149 (1923).

[13] Prasad, Shrivastava, and Gupta: Kolloid-Z, **37**, 101 (1925).

[14] Biltz and Geibel· Nachr. kgl. Ges. Wiss. Göttingen, **2**, 141 (1906).

[15] Linder and Picton: J. Chem. Soc., **61**, 133 (1892).

TABLE XXX

INFLUENCE OF CONCENTRATION ON THE COLOR OF Sb_2S_3 SOLS

Ratio H_2O/Sb_2S_3	Color
200	Deep red; clear in transmitted light, cloudy brown-red by reflected light
400	Raspberry red
600	Deep yellow-red
1,000	Reddish yellow to yellow
10,000	Yellow like dilute ferric chloride
100,000	Very light wine yellow
1,000,000	Faint yellow in layers at least 15 cm thick

of hydrosulfide and tartrate ions. When not dialyzed, it is more stable toward electrolytes than the corresponding arsenic trisulfide sol, but the stability can be varied through wide limits by varying the duration of the dialysis. On account of the similarity between the two sols, one might expect the order of electrolytes arranged according to their precipitating power to be approximately the same for both, as the experiments show.[16] Moreover, the effect of concentration of sol on the precipitation values of electrolytes containing cations of varying valence is similar to that for arsenic trisulfide sol.[17] The stability of antimony trisulfide sol decreases with age, and there is always more or less precipitation of the sulfide together with sulfur after standing for a long time. It is probable that the sol undergoes a photochemical decomposition similar to that observed with arsenic trisulfide sol (p. 176).

Jablczynski followed the velocity of coagulation of antimony trisulfide sol using a spectrophotometer. At first[18] the results seemed to be in accord with the Smoluchowski equation, but later[19] it was found necessary to modify the equation to fit the observations (*cf.* p. 201). Joshi[20] followed the course of the coagulation viscosimetrically and likewise showed that it did not follow Smoluchowski's equation. Ob-

[16] Schilow: Z. physik. Chem., **100**, 425 (1922); Iwanitzkaja, Orlowa, and Schilow: Kolloid-Beihefte, **18**, 1 (1923).

[17] Ghosh and Dhar: Kolloid-Z., **36**, 129 (1925).

[18] Jablczynski and Jedrzejowska: Bull. soc. chim., (4) **37**, 608 (1925).

[19] Jablczynski: Kolloid-Z., **54**, 164 (1931).

[20] Joshi and Prabhu: J. Indian Chem. Soc., **8**, 11 (1931); Joshi and Narayan: (Ray Commemorative Volume), 41 (1933); Joshi and Nanjappa: **11**, 133 (1934).

servations of the effect of changing the wall area in glass vessels indicate that the coagulation process is autocatalytic.[21]

COLLOIDAL ANTIMONY PENTASULFIDE AND TETRASULFIDE

Berzelius[22] first reported that antimony pentasulfide is formed by the action of hydrogen sulfide on a solution of antimonic acid. Bunsen[23] showed this to be true, provided the precipitation is effected by adding rapidly an excess of a saturated solution of hydrogen sulfide to the acid. This procedure was recommended by Bunsen for the quantitative estimation of antimony and for the separation of antimony and arsenic. Bunsen's observations were not confirmed by Wilm,[24] Mourlot,[25] and Thiele,[26] who found the precipitated sulfide to contain sulfur easily extractable with a sulfur solvent. Brauner[27] and later Bošek[28] did much toward clearing up the matter by showing that fairly pure pentasulfide is formed only when Bunsen's directions are followed exactly. Care must be taken to get all the antimony in the pentavalent state and to add the hydrogen sulfide solution rapidly in the cold to the antimonic solution containing 10 to 20% HCl. If the precipitation is accomplished by conducting hydrogen sulfide slowly into a solution containing but little hydrochloric acid, a part of the pentavalent antimony is reduced and the resulting precipitate is a mixture of pentasulfide, trisulfide, and sulfur.[29] In general, the reduction was found to be greater the slower the stream of hydrogen sulfide and the higher the temperature.

Schurmann and Böhm[30] obtained a fairly pure salt by passing hydrogen sulfide into a solution of antimony pentachloride containing 12 to 15% free HCl at a temperature not above −20°. The precipitate contained 15 to 30% sulfur which was extracted with carbon disulfide.

Pure antimony pentasulfide prepared by Bunsen's method is a rich orange in color when dried. Currie finds that heating has little visible effect on the compound until temperatures around 100° are reached,

[21] *Cf* Desai: Current Sci., **1**, 376 (1933)
[22] Pogg. Ann., **7**, 2 (1826); *cf., however,* Rose: **107**, 186 (1859).
[23] Ann., **192**, 305 (1878).
[24] Z. anal. Chem., **30**, 428 (1891).
[25] Compt. rend., **123**, 54 (1896).
[26] Ann., **263**, 371 (1891).
[27] Brauner and Tomicek: J. Chem. Soc., **53**, 145 (1888).
[28] J Chem. Soc., **67**, 515 (1895).
[29] Currie: J. Phys. Chem, **30**, 205 (1926).
[30] Kautschuk, **6**, 70, 91, 136 (1930).

when a dulling of the color is noted. At 135° the pigment darkens appreciably to a brown, and at 150° traces of black appear, indicating decomposition with the formation of black trisulfide. Carbon disulfide, chloroform, carbon tetrachloride, benzene, and toluene are without influence on the pure pentasulfide in the cold and have little effect at the boiling points of the several solvents.[31] Heating the sulfide causes it to lose sulfur to carbon disulfide in amount depending on the temperature. If heated between 70 and 75° it loses 1 atom of sulfur, leaving antimony tetrasulfide, Sb_2S_4, which starts to decompose slightly at 105° and rapidly at 155 to 160° giving Sb_2S_3.[32] Light acts slowly on the orange compound, converting it into black trisulfide.[33]

It is claimed that the best method of preparing antimony pentasulfide is to treat a solution of Schlippe's salt, $Na_3SbS_4 \cdot 9H_2O$, with dilute acids.[34] The product is never pure, containing, according to Klenker, Sb_2S_5, Sb_2S_3, and S in varying amounts, depending on the experimental conditions. This view was called in question by Kirchhof [35] and by Short and Sharpe,[36] who claimed that the so-called golden sulfide of antimony is the tetrasulfide, Sb_2S_4. This question was settled by Currie [29,37] who examined the golden precipitates obtained from thioantimonate under different conditions. Equal samples of the several preparations were treated with increasing amounts of sulfur solvent and allowed to stand at constant temperature until equilibrium was reached. The concentration of sulfur in the equilibrium solution was plotted against the composition of the residue expressed in milligrams of S in excess of Sb_2S_3, giving curves which indicate that the decomposition of thioantimonate by dilute acids yields no antimony pentasulfide but a mixture of sulfur and a solid solution of sulfur and antimony tetrasulfide.

Heating trisulfide with sulfur yields neither tetrasulfide nor pentasulfide.[29] Moreover, the trisulfide does not take up sulfur when kept in contact with sulfur solvents saturated with sulfur. It appears,

[31] Klenker: J. prakt. Chem., (2) **59**, 159 (1899); Esch and Balla: Chem.-Ztg., **28**, 595 (1904).

[32] Klenker: J. prakt. Chem., (2) **59**, 150 (1889); Luff and Porritt: J. Soc. Chem. Ind., **40**, 275*T* (1921); Dubosc: "Le Caoutchouc et la Gutta Percha," 8886, 8958 (1916).

[33] Brauner: J. Chem. Soc., **67**, 528 (1895).

[34] Abegg: Handbuch anorg. Chem., **3** (3), 620 (1907).

[35] Z. anorg. Chem., **112**, 67; **114**, 266 (1920).

[36] J. Soc. Chem. Ind., **41**, 109*T*; *cf., however,* Twiss: 171*T* (1922).

[37] *Cf.* Hansen: Angew. Chem., **45**, 505, 521 (1932).

therefore, that the equilibria $Sb_2S_5 \rightleftarrows Sb_2S_3 + 2S$ and $Sb_2S_4 \rightleftarrows Sb_2S_3 + S$ can be approached from one direction only, the side corresponding to the higher sulfide.

Antimony trisulfide and the tetrasulfide from antimonate appear amorphous to x-rays.[38]

A sol of antimony tetrasulfide from antimonate has been prepared using sodium "protalbinate" as protecting colloid. This sol may be sterilized by boiling and is recommended as a veterinary remedy in place of the antimonate.[39]

The golden sulfide is widely used as a pigment for rubber and as an assistant in the vulcanization process (p. 302).

COLLOIDAL BISMUTH TRISULFIDE

The Precipitated Salt

Bismuth trisulfide is thrown down as a brownish black hydrous mass on passing hydrogen sulfide into a solution of bismuth chloride that is not too strongly acid. No precipitate is obtained if the concentration is greater than 12% HCl and is incomplete in solutions stronger than 7.7%.[40] The sulfide is also precipitated from a bismuth chloride solution by sodium thiosulfate [41] and by thioacetic acid.[42] Adsorbed water is not removed completely from the sulfide until a temperature of approximately 200° is reached. Bismuth ion may be precipitated and weighed quantitatively as Bi_2S_3 provided the sulfide is heated for 1 hour in a stream of hydrogen sulfide.[43] At this temperature the apparently amorphous powder goes over rapidly to the crystalline form.[44] Bismuth trisulfide is much less soluble in alkali sulfides than the corresponding sulfides of arsenic and antimony,[45] but the solubility is not inappreciable.[46]

Schneider [47] claimed to get a hydrate of bismuth monosulfide, $BiS \cdot H_2O$, by treating a solution of bismuth tartrate, stannous chloride, and

[38] Currie: J. Phys. Chem, **30**, 237 (1926).
[39] Wolvekamp: U. S. Pat. 1,412,438 (1920).
[40] Ramachandran: Chem. News, **131**, 135 (1925).
[41] Vortmann: Monatsh., **7**, 418 (1886).
[42] Tarugi: Gazz. chim. ital., **27** I, 316 (1897).
[43] Moser and Neusser: Chem.-Ztg., **47**, 541, 581 (1923)
[44] Spring: Z. physik. Chem., **18**, 553 (1895).
[45] Stone: J. Am. Chem. Soc., **18**, 1091 (1896).
[46] Ditte: Compt. rend., **120**, 186 (1895); Stillman: J. Am. Chem Soc., **18**, 683 (1896).
[47] Pogg Ann., **97**, 480 (1856).

potassium hydroxide with hydrogen sulfide; but Vanino and Treubert [48] showed that the alleged compound was a mixture of hydrous bismuth trisulfide and bismuth. There appears to be no conclusive evidence of the existence of any sulfide of bismuth other than the trisulfide.[49]

Bismuth Trisulfide Sol

A sol results on passing hydrogen sulfide into a dilute solution of bismuth salt and dialyzing to remove excess electrolyte. Winssinger [50] employed a dilute bismuth nitrate solution treated with acetic acid and dialyzed 36 hours. The sol could be boiled without precipitation but was quite sensitive to the action of electrolytes. In thin layers the color was reddish brown and gave an absorption spectrum extending from the violet to the green and faintly into the red. Ozone precipitated the sol but was without action on the sulfide.[51]

COLLOIDAL STANNIC SULFIDE

The Precipitated Salt

Stannic sulfide is precipitated as a yellow gel by the action of hydrogen sulfide on an acidified solution of stannic chloride. The precipitate contains no stannous sulfide but may contain hydrous stannic oxide owing to hydrolysis of the chloride when the solution is quite dilute or but slightly acid.[52] It is probable that any oxide carried down would be converted to sulfide by prolonged action of hydrogen sulfide, since the gas converts a suspension of freshly formed stannic oxide into sulfide.[53] Stannic oxide sol peptized by hydrochloric acid is coagulated by hydrogen sulfide, but in this case the conversion to stannic sulfide is quite slow [54] because of the physical character of the oxide. By the action of hydrogen sulfide on stannic chloride under suitable conditions, Sisley and Meunier [55] claim to get a hydrate $SnS_2 \cdot 2H_2O$

[48] Ber., **32**, 1079 (1899).

[49] Aten: Z. anorg. Chem., **47**, 386 (1905); Herz and Guttmann: **53**, 63 (1907); **56**, 422 (1908); *cf., however,* Pélabon: J. chim. phys., **2**, 321 (1904); Compt. rend, **137**, 648, 920 (1903).

[50] Bull. soc. chim., (2) **49**, 452 (1888).

[51] Riesenfeld and Haase: Z. anorg. Chem., **147**, 188 (1925).

[52] Storch: Monatsh., **10**, 260 (1889).

[53] Scheerer: J. prakt. Chem., (2) **3**, 472 (1871).

[54] Jorgensen. Z. anorg Chem., **28**, 140 (1901); Barfoed: J. prakt. Chem., **101**, 368 (1867).

[55] Bull. soc. chim., (4) **51**, 939 (1932).

which is transformed to $SnS_2 \cdot H_2O$ at 120°; the evidence for the existence of the alleged hydrates is altogether inadequate.

The adsorbing power of stannic sulfide renders it unsuitable for the quantitative analysis of tin in certain solutions. Thus cobalt and nickel are carried down by the gel, the amount adsorbed varying inversely as the hydrogen ion concentration of the solutions.[56] The gel also adsorbs phosphate so strongly [57] that quite low results are obtained when the phosphate is estimated after the removal of tin as sulfide.[58]

If a stannic sulfide gel is allowed to remain in contact with ammonia, a solution results from which a voluminous white precipitate is obtained on acidification.[59] The same substance is formed by digesting stannic sulfide with ammonium carbonate solution, filtering, and acidifying. The dark red solution of stannous sulfide in ammonia becomes colorless on standing in the air, and from this, also, the white voluminous gel is precipitated by an acid. When freed from sulfur by washing with carbon disulfide the precipitate analyzes for hydrous stannic oxysulfide, $Sn_2S_3O \cdot xH_2O$. The freshly formed gel is readily soluble in ammonium carbonate, but, when aged by drying, it loses this property to some extent. If a dilute solution of the gel in ammonium carbonate is acidified with sulfuric acid and shaken until most of the carbon dioxide is removed, there results a very fine flocculent mass with a blue tinge. On washing with water, this gel is peptized, giving a sol with an acid reaction. Schmidt attributes the acidity of the sol to the presence of an acid, $Sn_2S_3O \cdot H_2O$ or $S(SnS \cdot OH)_2$; but it seems more likely that the acid reaction is caused by the presence of some sulfuric acid which cannot be washed out before peptization of the gel takes place.

Stannic Sulfide Sol

A sol of stannic sulfide, first described in 1839,[60] was prepared by the action of sulfur dioxide on a dilute acidified solution of stannous chloride. More recently it has been prepared by passing hydrogen sulfide into the sol of hydrous stannic oxide formed by dialysis of stannic chloride,[61] or by peptization with tartaric acid.[62] The most

[56] Auger and Odinot: Compt rend, **178**, 710 (1924).

[57] Kikuchi: J. Chem Soc. Japan, **43**, 329 (1922).

[58] Lord: Chem. News, **118**, 254 (1919); *cf.* Chandelle: Bull. soc. chim. Belg., **38**, 255 (1929).

[59] Schmidt: Kolloid-Z., **1**, 129 (1906).

[60] Hering: Ann Pharm., **29**, 90 (1839).

[61] Schneider: Z. anorg. Chem., **5**, 83 (1894).

[62] Dumanskii and Buntin: J. Russ Phys.-Chem. Soc., **61**, 279 (1929).

satisfactory method of preparation probably consists in peptizing the freshly formed gel by thorough washing.

COLLOIDAL LEAD SULFIDE

The Precipitated Salt

The brownish black precipitate of lead sulfide thrown down by hydrogen sulfide from slightly acid, neutral, and alkaline solutions of lead salts is said to be amorphous to x-rays, but electron diffraction studies show it to consist of extremely minute crystals.[63] Sloat and Menzies[64] measured the adsorption by the precipitated sulfide from 0.01 *M* solutions of several salts, for the purpose of investigating the relation between adsorption and lattice dimensions as well as solubility of the adsorbed substance. The results are given in Table XXXI.

TABLE XXXI

VARIATION OF ADSORPTION WITH LATTICE DIMENSIONS AND WITH SOLUBILITY

Salt	Adsorption mols/g PbS $\times 10^{10}$	Sum of ionic radii Å	Mol fraction solubility at 25°
LiBr	40 0	2 745	0 281
NaBr	43 0	2 97	0 141
NH_4Br	62 7	3 329	0 127
RbBr	82 7	3 43	0 111
CsBr	84 0	3 67	0 0949
KBr	126 7	3 285	0 0897
(PbS)		2 985	

It is apparent that the amount adsorbed does not depend on the ability of the adsorbed material to fit the space lattice of the adsorbent (*cf.* p. 115). Sodium bromide which has lattice dimensions nearest those of lead sulfide is, with the exception of lithium bromide, adsorbed the least. Ammonium bromide which belongs to the body-centered cesium chloride arrangement is adsorbed less than cesium bromide, in spite of the fact that ammonium bromide is capable of assuming the sodium chloride arrangement like lead sulfide and is a better fit than cesium bromide. Moreover, the amount adsorbed does not depend on the ability of the salt to orient on lead sulfide since the amount adsorbed

[63] Natta: Congr. intern. quim. pura aplicada, 9th Congr. Madrid, **2**, 177 (1934).

[64] J. Phys. Chem., **35**, 2022 (1931).

by the three unoriented salts, lithium, ammonium, and cesium bromides, is of the same order as the amount adsorbed by the other three salts which are known to be oriented.[65]

Comparing adsorption and mol fraction solubility of the salts, it will be seen that the amount adsorbed increases as the solubility falls off, indicating that in this instance solubility is a more important factor in adsorption than the lattice dimensions are.

By conducting hydrogen sulfide over many metallic salt solutions, films[66] of the various sulfides are formed on the surface (p. 235). The maximum thickness of such films of lead and bismuth sulfide on various concentrations of the nitrate solutions is 1500–2000 Å and is greater the more concentrated the solutions. With increasing thickness of film, the color changes from an olive brown to a red-brown.

Immig and Jander[67] showed that extremely small amounts of lead, cadmium, copper, silver, and bismuth can be estimated by conductometric titration with hydrogen sulfide using microchemical technique.

Lead Sulfide Sol

Lead sulfide sol may be prepared directly by the action of hydrogen sulfide on dilute solutions of lead salts,[50] especially the tartrate.[62] The use of the sol for the colorimetric estimation of small amounts of lead has been recommended.[68] A fairly stable sol results from the cathodic disintegration of galena;[69] but if sols of a high degree of stability are desired, some protecting colloid must be used. Lefort and Thibault[70] added hydrogen sulfide to a solution of lead acetate containing gum arabic; Menegazzi[71] used such protecting colloids as peptone, white of egg, and starch paste; and Chistoni and Milanesi[72] used denatured protein in preparing a sol which proved unsatisfactory for cancer treatment.

Brooks[73] prepared a stable sol of lead sulfide by the action of hydrogen sulfide on lead acetate solution containing 0.5% gelatin. The

[65] Sloat and Menzies: J. Phys. Chem., **35**, 2005 (1931).
[66] Mokruschin, Ginsburg, and Demjanova: Kolloid-Z., **75**, 10 (1936).
[67] Z. Elektrochem., **43**, 207 (1937).
[68] Lucas: Bull. soc. chim., (3) **15**, 39 (1896); Williams: J. Soc. Chem. Ind., **25**, 137 (1906); Ewan: **28**, 10 (1909); Harcourt: J. Chem. Soc, **97**, 841 (1910).
[69] Von Hahn: Kolloid-Z. (Zsigmondy Festschrift), **36**, 277 (1925).
[70] J. pharm. chim., (5) **6**, 169 (1882).
[71] J. Chem. Soc., **110** (1), 452 (1916).
[72] Arch. farmacol. sper., **46**, 147 (1929); Orestano: Boll. soc. ital. biol. sper., **7**, 263 (1932).
[73] J. Phys. Chem., **32**, 1717 (1928).

conversion to sol was 100% with a 0.25% solution of lead as the acetate; 50% with a 1.0% solution; and 3% with a 1.75% solution. This behavior was attributed to a decrease in the velocity of nuclei formation in more concentrated acetate solutions while the velocity of growth on nuclei remained unchanged (*cf.* p. 81). At 15°, the rate of combination of lead sulfide in the sol state and phosphate ions was found to be proportional to the surface of the unchanged particles, indicating that the reaction takes place between the surface and adsorbed phosphate ions, the adsorption of which is independent of the phosphate concentration over a wide range.

Lewis and Waumsley[74] made a deep brown opalescent sol by allowing lead to remain in contact with a solution of caoutchouc in 90% commercial benzene containing a small amount of carbon disulfide. The carbon disulfide acts on the lead, giving lead sulfide, which is protected by the caoutchouc. Any zinc or lead sulfide formed during the vulcanization of rubber in the presence of the metallic oxides is kept in the colloidal state by the rubber.[75]

[74] Kolloid-Z., **11**, 39 (1912); J. Soc. Chem Ind., **31**, 518 (1912).
[75] Martin and Davey: J. Soc Chem. Ind., **45**, 174*T* (1926).

CHAPTER XII

THE COLLOIDAL SULFIDES OF COPPER, SILVER, GOLD, AND THE PLATINUM FAMILY

COLLOIDAL CUPRIC SULFIDE

The Precipitated Salt

Copper sulfide precipitated at room temperature from cupric sulfate solution with hydrogen sulfide is almost pure CuS,[1] but after aging for 7 days under hydrogen sulfide solution it contains about 2% Cu_2S. If the precipitation is carried out at the boiling point, it contains approximately 5% Cu_2S, the amount increasing slightly on aging at room temperature. This behavior accounts for the variation in the composition of the precipitate reported by different people.[2] Sauer and Steiner [3, 4] believe that the product formed by the interaction of a cupric salt and hydrogen sulfide at room temperature is not cupric sulfide but cuprous sulfide plus an equivalent amount of sulfur and that cupric sulfide results only on heating the mixture. The experimental evidence for this opinion was derived from colorimetric observations of suspensions obtained by the interaction of both cuprous and cupric salts with hydrogen sulfide under varying conditions. Because of the similarity in color of cupric and cuprous sulfide, this evidence appears inconclusive. Kolthoff and Pearson [5] report that precipitates obtained with cupric salt and hydrogen sulfide, both in the hot and in the cold, give the same x-ray diffraction pattern. This was confirmed in the author's laboratory, and it was demonstrated further that the common pattern was from cupric sulfide and not from an equivalent mixture of cuprous sulfide and sulfur.

[1] Kolthoff and Pearson: J. Phys. Chem., **36**, 642 (1932); *cf.* Feigl Z anal. Chem., **72**, 32 (1927); Rossing: Z. anorg. Chem., **25**, 413 (1900); Jordis and Schweizer: Z. angew. Chem., **23**, 577 (1910); Coppock: Chem. News, **73**, 262 (1896); **76**, 231 (1897); Antony and Lucchesi: Gazz. chim. ital, **19**, 545 (1889).

[2] Thomsen: Ber., **11**, 2043 (1878); J. prakt. Chem., (2) **19**, 4 (1879); Brauner: Chem News, **74**, 99 (1896); Abel: Z. anorg. Chem, **26**, 411 (1901).

[3] Kolloid-Z, **72**, 41 (1935).

[4] *Cf.* Fischbeck and Dorner: Z. anorg. Chem., **182**, 228 (1929).

[5] J. Phys. Chem., **36**, 549 (1932).

Films[6] of copper sulfide from 1 to 25 molecules thick form on a copper sulfate solution in contact with hydrogen sulfide. Because of their metallic luster, films 2–3 molecules thick are visible and films 5–10 molecules thick are readily observed. The thinnest films are golden yellow and crystalline; thicker films appear dark brown to black. Hydrogen sulfide will not penetrate a film more than 60–80 Å in thickness. The films appear to be laminar systems composed of a succession of single monomolecular layers with adsorbed ions on their surfaces.[7] They are hydrophilic on the side next to the solution and hydrophobic next to the air. The contact angle of copper sulfide and water is zero in the absence of air.[8] If a fragment of copper or other metal above copper in the E.M.F. series is placed on the copper sulfide film, a secondary film of copper of the order of magnitude of 20 Å in thickness is formed below the sulfide.[9] The phenomenon is electrolytic, the following cell being set up: Cu | $CuSO_4$ solution | Cu.

Very finely divided copper sulfide, which dissolves in sulfuric acid giving hydrogen sulfide,[10] is formed by placing copper and sulfur in contact in a slightly acid solution of copper salt.[11] The color of the resulting precipitate is described as blue.[12] A precipitate subjected to 600 atmospheres pressure likewise has a blue metallic luster.[13] The mineral is black, bluish black, indigo blue, dark violet, or brown in appearance.

Rhythmic bands of cupric sulfide are formed when copper ion is allowed to diffuse into a gelatin jelly containing ammonium polysulfide.[14] The bands are white in color at the outset, but they gradually become darker, changing through green to brown. It seems unlikely that cupric sulfide should be white, and the initial white precipitate is doubtless sulfur; it is not observed if ammonium sulfide is substituted for the polysulfide.

Liesegang[15] placed a strong sodium chloride solution containing

[6] Mokruschin and Demjanova: J. Phys. Chem. (U.S.S R.), **5**, 1092 (1934); Kolloid-Z, **72**, 261 (1935); Mokruschin: **70**, 48 (1935).

[7] Mokruschin, Demjanova, and Konyaev: J. Phys. Chem. (U.S.S R), **6**, 100; Mokruschin and Vilesova: 640 (1935).

[8] DeWitt: J. Am. Chem. Soc., **57**, 775 (1935).

[9] Devaux: Compt. rend., **201**, 1305 (1935); **202**, 368; Cayrel. 926 (1936).

[10] Rieder: Z. Elektrochem., **8**, 370 (1902).

[11] Wicke: Ann., **81**, 241 (1852); Garelli: Rec. trav. chim., **42**, 818 (1923).

[12] Pélabon: Bull. soc. chim., (4) **51**, 377 (1932).

[13] Spring: Bull, acad. roy. méd. Belg., (3) **5**, 492 (1883)

[14] Hausmann: Z. anorg. Chem., **40**, 123 (1904).

[15] Z. angew. Chem., **36**, 229 (1923).

a little sodium sulfide in the bottom of a beaker; over this was placed a more dilute sodium chloride solution; and finally, a layer of very dilute cupric sulfate solution. After a time, the copper ion diffusing downward and the sulfur ion upward came in contact and formed a thin layer of cupric sulfide which gradually settled down. A process similar to this is believed to account for the copper sulfide deposit in certain lakes. In the salt water at the bottom of the lake, hydrogen sulfide is formed by the decay of organisms and by sulfur bacteria. During a flood, fresh water containing a little copper ion flows over this salt water. By diffusion, there is formed gradually a layer of copper sulfide which settles slowly to the floor of the lake.

Contamination by Zinc. Precipitated copper sulfide adsorbs hydrogen sulfide strongly, a circumstance which led Linder and Picton[16] to conclude that hydrosulfides such as $7CuS\ H_2S$ and $9CuS \cdot H_2S$ are formed. The sulfide thrown down by alkali sulfides is always contaminated more or less by adsorbed alkali salt.[17]

When copper sulfide is precipitated in the presence of zinc, the zinc is carried down in amounts depending on the concentration of zinc salt, the acid concentration, and the temperature. Kolthoff and Pearson[18] have shown that this contamination is not the result of coprecipitation,[19] direct adsorption, mixed crystal formation, or solid solution formation.[20] On the contrary, the zinc sulfide precipitates after the copper sulfide has been quantitatively formed; the contamination is therefore essentially a process of post-precipitation. The copper sulfide promotes the precipitation of zinc sulfide by virtue of its fine state of subdivision and the presence of an adsorbed layer of hydrogen sulfide on its surface. For example, when a mixture of copper and zinc sulfate is treated with hydrogen sulfide at room temperature in 0.36 *N* H_2SO_4 and filtered immediately after quantitative precipitation of the copper, all the zinc remains in solution. On the other hand, if the precipitate is allowed to stand before filtration, zinc separates on the precipitate as zinc sulfide, its amount increasing with

[16] J Chem. Soc., **61,** 120 (1892).

[17] Murmann: Monatsh., **17,** 706 (1896); Scheringa. Pharm. Weekblad, **57,** 1294 (1920).

[18] J Phys Chem, **36,** 549 (1932); Kolthoff and Moltzau· Chem. Rev, **17,** 293 (1935); *cf* Kolthoff and van Dijk: Pharm. Weekblad, **59,** 1351 (1922).

[19] Balarew, Gantschew, and Srebrow: Z. anorg. Chem., **165,** 192 (1927); Balarew and Kaischew· **167,** 237 (1927); Balarew: Kolloid-Beihefte, **30,** 249 (1930); Z anal. Chem, **102,** 408 (1935); Feigl: **65,** 25 (1924); Z. anorg Chem., **157,** 269 (1926); Bottger and Druschke: Ann., **453,** 315 (1927).

[20] Scheringa: Pharm. Weekblad, **55,** 431 (1918); **57,** 1294 (1920).

the time. Similarly when a zinc sulfate solution is brought in contact with precipitated copper sulfide more or less zinc sulfide precipitates on the copper sulfide surface.

Other things being equal, the amount of zinc sulfide post-precipitated in a given time decreases with increasing acidity.[21] This accounts for the analytical separation being made in strongly acid solution.[22] For the same acid normality, less post-precipitation was observed with hydrochloric acid than with sulfuric, because of the higher activity of hydrogen ion in the hydrochloric acid solution.

Other things being equal, copper sulfide precipitated at high temperatures was found by Kolthoff and Pearson to favor the post-precipitation of zinc much more than that thrown down at room temperature; hence, for the best separation, a higher acidity is necessary when the precipitation is effected at high temperatures. The sulfide formed at room temperature is black and easy to filter, whereas that formed at 100° is greenish in color, slimy, and hard to filter. If copper sulfide precipitated at room temperature is allowed to age under hydrogen sulfide before any zinc solution is added, its promoting effect on the precipitation of zinc is increased. Moreover, it assumes the same appearance as the sulfide formed at 100°, changing from black to greenish and becoming rather slimy and hard to filter.

To account for the above-mentioned variations in physical character which are responsible for the varying degrees of post-precipitation, it is necessary to know the combined effect of acidity, hydrogen sulfide concentration, and temperature on the primary and secondary particle size of the precipitate. The fact that the cold-precipitated salt aged under hydrogen sulfide assumes the properties of the hot-precipitated salt indicates (1) that the primary particle size does not vary widely with the temperature of precipitation and (2) that the cold-precipitated salt forms dense aggregates having a lower effective surface which is increased on standing by the peptizing action of hydrogen sulfide. X-ray analysis disclosed that the different precipitates had the same crystal structure, but the work should be repeated to determine from the width of the diffraction lines whether the primary particle size varies appreciably with the conditions of precipitation.

The increased reactivity of zinc ions to form zinc sulfide at the

[21] *Cf.* Bottger and Druschke: Ann., **453**, 315 (1927).

[22] Larsen: Z. anal. Chem, **17**, 312 (1878); Berglund: **22**, 184 (1883); *cf.* Baubigny: Compt. rend, **94**, 1183, 1251, 1473, 1595 (1882); **95**, 34 (1883); **105**, 751, 805 (1887); **107**, 1148 (1888); **108**, 236, 450 (1889); Glixelli: Z. anorg. Chem., **55**, 297 (1907).

surface of copper sulfide is probably the result of the greater tendency of adsorbed hydrogen sulfide to ionize as compared with hydrogen sulfide in the bulk of the solution. Cystine, thiophenol, and thiobarbituric acid accelerate the precipitation of zinc sulfide alone but they strongly retard the post-precipitation on copper sulfide, probably because they are so strongly adsorbed that they displace or prevent the adsorption of hydrogen sulfide.

Finely divided substances such as glass powder, silica gel, barium sulfate, charcoal, sulfur, talcum, aluminum oxide, and filter paper likewise promote the precipitation of zinc sulfide. Kolthoff and Pearson cite this behavior to show the general character of the surface effect upon the speed of formation of a precipitate from a supersaturated solution.

Metallic Conduction of Copper Sulfide. Solid cupric sulfide is a relatively good conductor of electricity, Bädeker [23] finding the specific resistance at ordinary temperature to be 0.000125 when that of copper is 0.0000017 and that of bismuth is 0.000115.[24] Thus cupric sulfide is almost as good a conductor as bismuth. Hittorff [25] and Bodländer and Idaszewsky [26] observed no migration of copper ions during the passage of the current and concluded therefore that the salt conducts like a metal and not like an electrolyte. Cuprous sulfide is likewise a conductor, but the bulk of the evidence indicates that it conducts electrolytically.[27] Bodländer attributes the slight conductivity of cuprous sulfide at room temperature to the presence of a small amount of cupric sulfide. He states further that, at 110°, cuprous sulfide becomes an electrolyte but the electrolysis produces cupric sulfide at the anode, the metallic conductivity of the cupric gradually replacing the electrolytic conductivity of the cuprous sulfide.

A completely satisfactory explanation of metallic conduction in compounds such as cupric sulfide is not yet available. Trümpler [28] measured the potential of a number of solid conducting salts against a saturated solution containing the negative component of the salt in the

[23] Ann. Physik, (4) **22**, 749 (1907).

[24] Giebe: Dissertation, Berlin (1903).

[25] Pogg Ann., **84**, 1 (1851).

[26] Z. Elektrochem., **11**, 161 (1905).

[27] Hittorff: Pogg. Ann., **84**, 1 (1851); Kohlrausch: Wied. Ann., **17**, 642 (1882); Bidwell: Phil. Mag., (5) **20**, 328 (1885); Mönch: Neues. Jahrb. Mineral. Geol., **20**, 365 (1905); von Hasslinger: Monatsh., **28**, 173 (1907); Trümpler: Z. physik. Chem., **99**, 9 (1921); Tubandt, Eggert, and Schibbe: Z. anorg. Chem., **117**, 1 (1921).

[28] Z. physik. Chem., **99**, 9 (1921)

free and ionic state. From the different behavior of metal-like and electrolytic conductors with respect to the influence of the negative component on the potential, a fundamental difference in internal structure is deduced. Thus it is assumed that, in pure metallically conducting compounds, the space lattice points are occupied by atoms or molecules but not by ions; hence such compounds appear to be non-polar, in contradistinction to electrolytic conductors. This assumption may be true, but it is not very helpful since it offers no explanation of the fact that metallic conductivity obtains with only a few salts. Moreover, it does not account for the very much greater metallic conductivity of cupric sulfide than of other salts of the same kind. Since Bridgman [29] has prepared a modification of phosphorus possessing metallic properties, it may be that a similar form of sulfur exists and that cupric sulfide is a compound of copper with this metallic form of sulfur.

The Electrocapillary Phenomenon of Becquerel. If copper nitrate solution is placed in a cracked test tube immersed in a beaker of sodium sulfide solution, keeping the two liquids at the same level, copper sulfide first forms in the cracks and is followed by the appearance of crystals of copper on the copper nitrate side and of a yellow layer of solution containing polysulfide on the other side. Becquerel,[30] who first observed this phenomenon, believed it to be connected in some way with electroendosmose.[31] Thirty years after Becquerel's discovery Braun [32] passed a high-potential current through capillaries such as cracked glass, using heavy metal solutions, and observed a deposition of metal on the side of the capillary turned toward the positive pole. This phenomenon, called "electrostenolysis," is similar in certain respects to the Becquerel phenomenon, and Coehn [33] believes it to be closely connected with electroendosmose.

It is well known that colloidal particles will migrate in an electric field in a direction depending on their charge; this is known as cataphoresis. If the particles are kept stationary, in other words, if a porous diaphragm of the particles separates the anodic and cathodic solutions an impressed potential will cause the liquid to move in a direction

[29] J Am. Chem. Soc., **36**, 1344 (1914); **38**, 609 (1916).

[30] Compt. rend, **64**, 919, 1211; **65**, 51, 62, 720 (1867); **66**, 77, 245, 766, 1066; **67**, 1081 (1868); **71**, 197 (1870); **74**, 1310 (1872); **76**, 245 (1873); **78**, 1081; **79**, 82, 1284 (1874); **80**, 585 (1875); **82**, 354 (1876); **84**, 145; **85**, 169 (1877).

[31] *Cf., however,* Ostwald: Z. physik. Chem, **6**, 71 (1890).

[32] Wied. Ann., **42**, 450 (1891); **44**, 473 (1892).

[33] Z. Elektrochem., **4**, 501 (1898); Z. physik. Chem., **25**, 651 (1898); Holmes: J. Am. Chem. Soc., **36**, 784 (1914).

depending on the sign of the diaphragm charge which, in turn, depends on the nature of the ion preferentially adsorbed by the diaphragm.[34] This phenomenon is called electroendosmose. The inner walls of the capillary in contact with the liquid are coated with an electrical double layer. With a glass capillary, the stationary layer on the glass is negatively charged as a rule, owing to preferential adsorption of anions, whereas the movable layer in the liquid contains an excess of cations and so is positively charged. Under the influence of an electric current of sufficient voltage, the positively charged movable side of the double layer is torn away, leaving the end of the capillaries toward the anode charged negatively. On these cathodic points metal will deposit only in small amounts as a rule; first, because of the relatively small charge on the capillary wall, and second, because the minute deposit takes part in the conduction, one end becoming anode and losing as fast as the cathode end gains. But, as Coehn points out, the quantity of metal can grow under certain conditions: first, if the metal is noble; second, if an insoluble compound, especially a peroxide, is formed at the anode side; and third, if the discharged anion, instead of dissolving the metal, oxidizes "ous" to "ic" salts in the solution.

Freundlich[35] points out that in Becquerel's experiment the two sides of the glass capillary will be oppositely charged by contact with the oxidizing and reducing solutions on the two sides. Now, as already noted, copper sulfide is first formed in the capillary, and this salt is a fairly good metallic conductor. Local currents will therefore be formed which flow in one direction through the capillaries and in the opposite direction through the copper sulfide as well. Just as in electrostenolysis, an appreciable amount of metal can form on the cathodic portion of the capillary provided the conditions referred to above obtain.

Cupric Sulfide Hydrosols

The sol of cupric sulfide was first mentioned by Wright,[36] who prepared it by treating the precipitated salt with insufficient potassium cyanide for complete solution, filtering and washing the residue which

[34] Perrin· J chim. phys., **2**, 601 (1904); Bethe and Toropoff: Z physik. Chem, **88**, 686 (1914); **89**, 597 (1915); Girard; J. chim phys, **17**, 383 (1919); Girard and Platard: Compt. rend., **178**, 1212 (1924); Gyemant· Kolloid-Z., **28**, 103 (1921).

[35] "Kapillarchemie," 2nd ed, 371 (1922); Kolloid-Z., **18**, 11 (1926); Freundlich and Sollner· Z physik. Chem., **A138**, 349 (1928); **A152**, 313 (1931); *cf.* Bikerman: **A153**, 451 (1931)

[36] J. Chem. Soc., **43**, 163 (1883).

was promptly peptized. Spring [37] first obtained a stable sol by washing the precipitated sulfide with hydrogen sulfide water until peptization was complete. The sol was brown when dilute and black with a slight greenish fluorescence when concentrated. It withstood boiling without precipitation but was quite sensitive to the presence of salts. The amorphous residue obtained on evaporating to dryness had the appearance of a black varnish. It was not peptized by washing even when the drying was done at ordinary temperatures. Linder and Picton [16] suspended hydrous cupric oxide in water through which hydrogen sulfide was passed until the oxide was converted into sulfide and peptization was complete, 5 days being required. Young and Neal [38] started with suspended copper carbonate instead of the hydrous oxide.

Muthmann and Stutzel [39] made a fairly stable sol by passing hydrogen sulfide into a solution of potassium cupri thiosulfate, $K_2Cu(S_2O_3)_2$. Lottermoser [40] obtained a very much more satisfactory preparation by treating a saturated solution of copper glycocoll with hydrogen sulfide. When the procedure was carried out in the cold, the sol was clear brown in color and was made up of very finely divided particles; when carried out in the boiling solution, the color was a deep olive green and the particles were distinctly larger. The brown sol formed in the cold was changed to green by heating. The presence of glycocoll has a marked stabilizing influence on the sol, just as succinimide protects hydrous cupric oxide sol formed by hydrolysis of copper succinimide.[41]

Stable sols result by the interaction of cupric salt and hydrogen sulfide in the presence of gelatin [42] or gum arabic [3] as protecting colloid. In accord with Lottermoser's observation, sols formed in the cold are brownish in color and change to greenish on heating. Since the sols formed by the action of hydrogen sulfide on cuprous salt in the presence of gum arabic are brownish and do not change their color on heating, Sauer and Steiner [3] conclude that the brown sol obtained with a cupric salt in the cold is an equivalent mixture of cuprous sulfide and sulfur and not cupric sulfide. As already indicated, this question may be settled definitely by obtaining x-ray diffraction pat-

[37] Ber, **16**, 1142 (1883).
[38] J. Phys Chem, **21**, 14 (1917).
[39] Ber, **31**, 1734 (1898).
[40] J. prakt. Chem., (2) **75**, 293 (1907).
[41] Ley: Ber, **38**, 2199 (1905).
[42] Meneghetti: Boll soc. ital. biol. sper., **4**, 613 (1929).

terns of the respective products. Warming a mixture of protected copper sol and sulfur sol gives a stable cupric sulfide sol.[43]

The removal of the excess hydrogen sulfide from sols prepared by the method of Spring, or of Linder and Picton, decreases their stability appreciably.[44] On the other hand, an excess of hydrogen sulfide is said to decrease the precipitation value of certain electrolytes for the sol.[45] The relative precipitating powers of potassium chloride, calcium chloride, and aluminum chloride are in the approximate ratio 1:39:875.

The sulfides of copper and mercury are obtained in the sol state by subjecting suspensions of the salts to the action of the silent electric discharge.[46] The peptizing action is attributed to hydrogen sulfide formed by reduction of the metallic sulfides.

Peskov[47] observed the same lyotropic influence of the cation of neutral alkali salts on the solution of colloidal cupric sulfide as already noted with colloidal arsenic trisulfide (p. 180).

Cupric Sulfide Organosols

Organosols of cupric sulfide are obtained by passing hydrogen sulfide into dilute solutions of copper salts in an organic solvent. Naumann[48] obtained a pyridine sol by the action of dry hydrogen sulfide on a dilute solution of copper chloride in pyridine; Lottermoser[49] made an alcosol from a solution of copper glycocoll in absolute alcohol and an ether sol from a solution of copper acetoacetic ester in ether; and Errera[49] prepared an alcosol from a solution of copper acetate in absolute alcohol. In general, the organosols are most stable when quite dilute, but Errera's alcosol was quite stable although it contained 38.7 g CuS/l.

Errera observed the time required to coagulate alcosols of mercuric sulfide, cupric sulfide, and platinum by the addition of liquids of varying dielectric constant, D. One cubic centimeter of the alcosol containing 38.7 g CuS/l was added to 6 cc of the several liquids and the observations made as recorded in Table XXXII. Experiments were also carried out with mixtures of the several liquids with varying

[43] Sauer and Steiner: Kolloid-Z., **72**, 35 (1935).
[44] Young and Neal: J. Phys. Chem., **21**, 18 (1917).
[45] Mukherjee and Sen: J. Chem. Soc., **115**, 461 (1919).
[46] Miyamoto: J. Chem. Soc. Japan, **56**, 1359 (1935); Kolloid-Z., **74**, 32 (1936).
[47] Kolloid-Z., **32**, 24, 163 (1923).
[48] Ber., **37**, 4612 (1904).
[49] Kolloid-Z., **32**, 240 (1923).

TABLE XXXII

ACTION OF LIQUIDS ON CUPRIC SULFIDE ALCOSOL

Liquid	*D*	Observations
Water	81	Milky in 30 min., no further change in 127 hr.
Nitrobenzene	35.5	No change in 127 hr.
Methyl alcohol	33 0	No change in 127 hr.
Ethyl alcohol	25.0	No change in 127 hr.
Acetone	21.0	No change in 127 hr.
Isobutyl alcohol	18 6	No change in 127 hr.
Isoamyl alcohol	5 7	No change in 127 hr.
Amyl acetate	5 6	No change in 127 hr.
Chlorobenzene	5.57	Partial coagulation in 8 min,; complete in 3 5 hr.
Chloroform	4 95	Partial coagulation in 96 hr.; incomplete in 126 hr
Ether	4 36	Partial coagulation in 10 min.; complete in 3 5 hr.
Benzene	2 29	Partial coagulation in 96 hr.; incomplete in 126 hr.
Xylene	2 5	Incomplete coagulation in 7 min.; complete in 3 5 hr.
Hexane	1 85	Complete in 1 min.
Carbon tetrachloride	2 25	Incomplete in 1 min.; complete in 3 5 hr.

quantities of ethyl alcohol. The addition of liquids having a dielectric constant greater than the dispersing medium has no coagulating effect on the sol, whereas liquids with a dielectric constant smaller than that of the dispersing medium coagulate the sols, and usually, the smaller the dielectric constant, the greater is the coagulating power of the added liquid. In general, if the dielectric constant of the dispersed phase is greater than that of the dispersing liquid, the addition of a second liquid of lower dielectric constant increases the difference between the dielectric constant of the two phases, thereby rendering the sol more stable. On the other hand, if the dispersed phase has the lower dielectric constant and if the dielectric constant of the medium is further decreased, two cases exist: (1) the difference in dielectric constant is slight, the initial additions decreasing the stability to a minimum followed by an increase in stability with further additions; (2) the dispersing phase may have a very low dielectric constant, additions lowering the stability both by decreasing the difference between the dielectric constant of the media and by lowering the charge on the submicrons. Cupric sulfide alcosol is negatively charged both alone and when mixed with ten times its volume of benzene. Agglomeration of the colloidal particles is always accompanied by the distinct color change from dark brown to a bright olive green.

COLLOIDAL CUPROUS SULFIDE

A brown sol of cuprous sulfide is said to form on mixing a cuprous ammonium chloride solution with hydrogen sulfide when the ratio of copper to sulfur in the interacting solution is 2 to 1. A similar sol results by the interaction of copper and sulfur sols in the proper proportions; with sulfur in excess the first product is cuprous sulfide.[3, 43] All these preparations should be examined by x-rays to determine whether they are chiefly cuprous sulfide or cupric sulfide.

When a solution of sodium cupri thiosulfate is acidified, there is a period of induction followed by the appearance of what is described as red cuprous sulfide sol.[50] This subsequently precipitates, giving a blood-red gel which turns successively brown, deep brown, greenish black, and finally black. The length of the induction period depends on the nature and concentration of the acid and the concentration of sodium cupri thiosulfate. The chief cause of the phenomenon is the formation of colloidal sulfur, which inhibits the precipitation process. The use of ozonized hydrochloric acid, nitric acid, or perchloric acid, which oxidize colloidal sulfur, cuts down the induction period. With a constant amount of acid and sodium cupri thiosulfate, the presence of increasing amounts of sodium thiosulfate decreases the induction period up to a certain point and then increases it. The hastening is attributed to the coagulating influence of the added salt on the colloidal sulfur; and the subsequent retarding at higher salt concentrations, to the destruction of acid.

Svedberg[51] prepared a sol of cuprous sulfide in isobutyl alcohol by electrical disintegration of the mineral, copper glance.

COLLOIDAL SILVER SULFIDE

The Precipitated Salt

Silver sulfide is precipitated as a black amorphous powder by the action of hydrogen sulfide or a soluble sulfide on a solution of silver oxide or salt. The precipitate from neutral silver nitrate solution always contains adsorbed sulfur which cannot be removed by carbon disulfide.[52] Hantzsch[53] claims to have prepared silver disulfide, Ag_2S_2, as a brown amorphous powder by adding a solution of sulfur

[50] Sambamurty: Proc. Sci. Assoc. Maharajah's College, Vizianagaram, Dec. 10 (1922); Chem. Zentr., I, 1414 (1923).

[51] "Die Methoden zur Herstellung Kolloider Lösungen," 490 (1909).

[52] Kohlschütter and Eydmann: Ann., **390**, 347 (1912).

[53] Z. anorg. Chem., **19**, 104 (1899).

in carbon disulfide to a solution of silver nitrate in benzonitrile. If solvents other than benzonitrile are used, silver sulfide is obtained. Since the failure of carbon disulfide to extract sulfur from the alleged disulfide is the chief evidence in support of its chemical individuality, there may be some question whether it is a true compound or a solution of silver sulfide and sulfur.

Silver sulfide is formed by the action of moist hydrogen sulfide on metallic silver. According to Gans[54] the reaction proceeds rapidly at first, slows down after 200 hours, increases again after 500 hours, and then continues at approximately constant velocity. It is suggested tentatively that the decrease in velocity after 200 hours is caused by the formation of a protecting layer of amorphous sulfide which is subsequently ruptured or crystallizes, allowing the surface action to proceed more rapidly. This hypothesis should be tested experimentally by examining the protecting layer of sulfide by means of electron diffraction. Silver sulfide has been synthesized by the action of pure sulfur vapors on pure silver for the purpose of estimating the atomic weight of sulfur.[55]

Unlike cupric sulfide, which is a pure metallic conductor, β-silver sulfide stable below 179° is a mixed conductor, about 80% of the current being carried by silver ions and 20% being conveyed as in a metallic conductor; the α modification, stable above 179°, is a pure electrolytic conductor.[56]

Silver Sulfide Sol

Preparation. The most stable hydrosols of silver sulfide are obtained by precipitating the salt in the presence of protecting colloids such as gum arabic,[57] casein,[58] albumin, dextrin, gelatin, and glue.[59] Paal and Voss[60] prepared very stable sols using a salt of protalbinic or lysalbinic acid as protecting colloid. One gram of sodium "protalbinate" in 15 cc of water is treated with an equivalent amount of silver nitrate; the precipitate of silver "protalbinate" is suspended in water and treated with ammonium sulfide. The sol of silver sulfide

[54] Z physik Chem., **109**, 49 (1924).

[55] Honigschmid: Z. Elektrochem., **36**, 689 (1930); Honigschmid and Sachtleben: Z. anorg. Chem., **195**, 207 (1931).

[56] Tubandt, Eggert, and Schibbe: Z. anorg. Chem., **117**, 1 (1921); *cf* Trumpler: Z. physik. Chem., **99**, 9 (1921).

[57] Lefort and Thibault: J. pharm. chim., (5) **6**, 169 (1882)

[58] Muller and Artmann: Oesterr. Chem.-Ztg., **7**, 149 (1904).

[59] Stiasny: Gerber, **33**, 124 (1907); Chem Zentr., II, 489 (1907).

[60] Ber., **37**, 3862 (1904).

which results is dialyzed to remove excess electrolyte and evaporated to dryness in a vacuum desiccator. The residue is readily peptized by water, giving a stable sol of any desired strength.

Freundlich and Nathansohn [61] obtained a silver sulfide sol by mixing Carey Lea's silver sol with a sulfur sol. Both sols are negatively charged, and the interaction takes place at the surface of the micelles. The transformation is accompanied by changes in color: brown, wine red, violet, steel blue, greenish blue, greenish brown, and finally a pale yellowish brown. The color changes result from the presence of varying amounts of silver, sulfur, and silver sulfide, in the micelles, as in the photo-chlorides (Vol. I, p. 121). A mixture of a solution of hydrogen sulfide and colloidal silver goes through similar color changes, finally giving colloidal silver sulfide.

Color. A stable sol of silver sulfide may be obtained without the use of protecting colloids by adding hydrogen sulfide or sodium sulfide to a dilute solution of silver nitrate. If the solution is as dilute as 0.002 *N*, a stable yellow sol results [62] which passes through a range of colors from yellow to green on adding electrolytes.[63] Some observations are recorded in Table XXXIII. Five-cubic-centimeter portions

TABLE XXXIII

COLOR CHANGES IN THE COAGULATION OF SILVER SULFIDE SOL BY ELECTROLYTES

Salt	Concentration m.eq./l	Color	Salt	Concentration m.eq./l	Color
KCl	60	Yellow	KNO_3	100	Violet
KCl	80	Ice blue	KNO_3	120	Brown-red
KCl	90	Blue	$MgSO_4$	10	Yellow
KCl	100	Violet	$MgSO_4$	20	Violet
HCl	80	Yellow	$MgSO_4$	40	Blue
HCl	100	Blue	$MgSO_4$	80	Dull green
HCl	120	Violet	$Al_2(SO_4)_3$	1 5	Leaf green
HCl	140	Dull green	$Al_2(SO_4)_3$	2 4	Blue
KNO_3	60	Dull green	$Al_2(SO_4)_3$	3.0	Red
KNO_3	80	Ice blue	$Al_2(SO_4)_3$	3.6	Dull green

[61] Kolloid-Z., **29**, 16 (1921).

[62] Odén: Nova Acta Regiae Soc. Sci. Upsaliensis, (4) **3**, 4 (1913); *cf.* Winssinger: Bull. soc. chim., (2) **49**, 452 (1888); Lottermoser: J. prakt. Chem., (2) **72**, 39 (1905).

[63] Von Hahn: Kolloid-Z., **27**, 172 (1920).

of the colloid were mixed with 5 cc of electrolyte of varying concentrations, expressed in milliequivalents per liter (m.eq./l) in the final volume, and the color noted after standing 5 minutes. The color is seen to depend on the concentrations of electrolyte between fixed limits; thus, for potassium chloride no change takes place below 60 m.eq./l, and the color is always brownish red above 110 m.eq./l. The stability at the above stages of agglomeration is not great, and complete coagulation results in a few hours. The precipitate is always dark brown, but, if shaken with the solution from which it separates, the suspension appears bluish from the blue and violet sols and reddish from the red and dull green sols.

The age of the sol has a marked influence on the variety of the color changes during the flocculation of the sol; *e.g.*, 5 hours after preparation no blue or green colors can be obtained, and after 7 hours, no violet color. If allowed to stand 24 hours the sols change directly from yellow to reddish brown.

The results indicate that the micelles of the sol increase in size spontaneously at least during the first 24 hours. Secondary particles of a wide variety of sizes may be produced by partial agglomeration of fresh sols with varying amounts of electrolytes. The difference in size of the secondary aggregates is probably the chief cause for the wide variety of colors observed. It is a mistake, however, to conclude *a priori* that the variation in color is caused entirely by the size of the micelles. Thus, colloidal gold sols [64] can be obtained which are red, violet, or blue by transmitted light, and colloidal silver sols [65] which are yellow, red, or blue; in general, the micelles of the blue sols are larger than the red, but this is not always true (*cf.* Vol. I, p. 79).

The appearance of the violet color in the flocculation of fresh sols is so sharp that von Hahn [66] compared the stability of sols prepared under different conditions by means of the "violet value" which was taken arbitrarily as the concentration of electrolytes which is just sufficient to produce a certain shade of violet after 5 minutes' standing (44, according to Ostwald's color scale). The stability of the sol was found to increase with (1) length of time of treatment with hydrogen sulfide, (2) more rapid passing of hydrogen sulfide through the solution, and (3) higher temperatures of formation. In general, the optimum conditions for stability are those which cause the maximum rate of precipitation and hence the greatest degree of dispersion. Von

[64] Faraday: Phil. Trans, **147**, 145 (1857).
[65] Lea: Am. J. Sci., (3) **37**, 476 (1889).
[66] Kolloid-Z., **29**, 139 (1921).

Hahn's observations agree with those of Boutaric and Vuillaume on arsenic trisulfide sol already referred to (p. 172).

The "violet value" for different electrolytes gives the order of their precipitating power. From Table XXXIII the ratio $Al_2(SO_4)_3$: $MgSO_4$: KCl: HCl is approximately 1: 10: 50: 70.

Pieroni [67] prepared a pyridine organosol of silver sulfide by treating a solution of silver nitrate in pyridine with hydrogen sulfide dissolved in pyridine.

COLLOIDAL SULFIDES OF GOLD

Gold monosulfide is formed by passing hydrogen sulfide into a solution of aurous cyanide in potassium cyanide and then acidifying with hydrochloric acid. The finely divided steel-gray mass must be washed with water containing dilute hydrochloric acid; otherwise it is peptized, forming a perfectly clear sol.[68] When dried it yields a brownish-black powder that cannot be peptized. A sol is obtained also by saturating with hydrogen sulfide a solution of aurous cyanide in potassium cyanide,[69] adding a little hydrochloric acid, and warming carefully until a brown turbidity is produced. On dialysis a stable deep-brown sol results which can be separated from the heavy undissolved sulfide by decantation and filtration.

A so-called auro-auric sulfide, Au_2S_2, is said to form when hydrogen sulfide is passed into a cold neutral solution of auric chloride;[70, 71] but Gutbier and Durrwächter,[72] unable to obtain the compound by this method, question its individuality. Whatever the substance may be, it is readily obtained in colloidal solution. Winssinger [73] added hydrogen sulfide to a solution of auric chloride as nearly neutral as possible and secured a sol containing 0.55 g of sulfide per l which was stable for several weeks. Schneider [69] made a more concentrated sol by treating the freshly precipitated sulfide with insufficient potassium cyanide or ammonium polysulfide for complete solution, suspending the residue in water, and dialyzing. After the electrolyte concentration was reduced below a critical value, the suspended particles were peptized, giving a stable sol that was clear in both transmitted and re-

[67] Gazz. chim. ital, **43** I, 198 (1913).

[68] Hoffmann and Kruss Ber., **20**, 2369 (1887).

[69] Schneider: Ber., **24**, 2241 (1891).

[70] Hoffmann and Krüss: Ber., **20**, 2204 (1887); Ditte: Compt. rend, **120**, 320 (1895).

[71] Antony and Lucchesi: Gazz. chim. ital., **19**, 545 (1889).

[72] Z. anorg. Chem., **121**, 266 (1922).

[73] Bull. soc chim., (2) **49**, 452 (1888).

flected light. The precipitate formed by agglomerating the sol was reddish brown when moist and black when dry.

An alcosol was prepared by mixing the hydrosol with three times its volume of alcohol, followed by dialyzing against absolute alcohol to remove the water. The alcosol was similar in appearance to the hydrosol but more stable.

On account of the alleged instability of Au_2S_3 in the presence of water, this salt was first prepared in the dry way or precipitated from non-aqueous media. Thus Antony and Lucchesi [71] passed dry hydrogen sulfide over lithium auric chloride at $-10°$, and Hofmann and Höchtlen [74] precipitated the compound as a dark brown mass by the interaction of auric chloride and hydrogen sulfide in absolute ether. Gutbier and Durrwachter [72] claim to get Au_2S_3 instead of Au_2S_2 by passing a rapid stream of hydrogen sulfide into an aqueous solution of gold chloride at $-2°$. With a slow stream of hydrogen sulfide at 100° the trisulfide first formed reacts with the excess of gold chloride giving metallic gold. The precipitate obtained under intermediate conditions is said to be a mixture of Au_2S_3 and Au, no Au_2S_2 being formed by any modification of the procedure. These observations raise the question of the individuality of Au_2S_2 and suggest that the alleged Au_2S_2 precipitate and sol referred to in a preceding paragraph are mixtures of Au_2S_3 and Au. An Au_2S_3 sol may be prepared in concentrated phosphoric acid (p. 174).

THE COLLOIDAL SULFIDES OF THE PLATINUM FAMILY

Of the sulfides of the platinum family of elements, PdS, OsS_4, Ir_2S_3, and PtS_2 are known to form colloidal solutions. The sols of palladium monosulfide, osmium tetrasulfide, and platinum disulfide are obtained by conducting hydrogen sulfide into dilute solutions of palladous chloride, osmium tetroxide, and platinic chloride, respectively.[73] Of these sols, platinum disulfide is the most readily formed and the most stable. Indeed, the tendency of the salt to go into the colloidal state is so great that electrolytes such as magnesium chloride must be added to the solution before conducting in hydrogen sulfide in the estimation of platinum as sulfide.[75] Freshly formed iridium sesquisulfide, thrown down from a solution of the oxide by hydrogen sulfide, is carried into colloidal solution by thorough washing.[76]

[74] Ber, **37**, 245 (1904).

[75] Ivanov: J. Russ. Phys.-Chem. Soc., **48**, 527 (1916); Gaze: Chem. Zentr, I, 464 (1913).

[76] Berzelius: "Lehrbuch der Chemie," 3rd ed., **3**, 222 (1834).

CHAPTER XIII

THE COLLOIDAL SULFIDES OF ZINC, CADMIUM, AND MERCURY

COLLOIDAL ZINC SULFIDE

The Precipitated Salt

Zinc sulfide is obtained by precipitating neutral, slightly acid, or alkaline solutions of zinc salts by hydrogen sulfide or alkali sulfides. Four gels formed at room temperature by precipitating normal zinc sulfate with hydrogen sulfide in the presence of (1) sodium hydroxide, (2) ammonium hydroxide, (3) acetic acid, and (4) no foreign electrolyte, were all found by Levi and Fontana [1] to be crystalline to x-rays, giving the sphalerite diffraction pattern. This was confirmed and extended in the author's laboratory by Milligan and Ekholm starting with various zinc salts: sulfate, nitrate, chloride, bromide, iodide, and acetate. The different behavior of zinc sulfide precipitates obtained during analytical procedures depends on varying states of aggregation since the primary particle size is approximately the same irrespective of the *p*H value of the solution from which the sulfide separates. Digestion for several days on the water bath gives preparations that show sharp interference lines in the x-ray diffraction pattern. The crystals are submicroscopic, for Allen, Crenshaw, and Merwin [2] found no microscopic evidence of crystalline structure in any gel precipitated and digested under ordinary laboratory conditions. Microscopic crystals are formed only by prolonged digestion of the gel in platinum tubes with sodium sulfide or sulfuric acid in the presence of an excess of hydrogen sulfide at temperatures varying from 200 to 350°. The crystals obtained by digestion with sodium sulfide are always the common sphalerite or blende whereas both sphalerite and wurtzite are formed in the digestion with acid. At a given temperature the amount of wurtzite formed is greater the higher the acid concentration, and at a given acid concentration the amount of sphalerite is greater the higher the temperature.

[1] Atti accad. Lincei, (6) **7**, 502 (1928); *cf.* Böhm and Niclassen Z. anorg. Chem., **132**, 1 (1924).

[2] Allen, Crenshaw, and Merwin: Am. J. Sci, (4) **34**, 351 (1912).

Owing to the solubility of gelatinous zinc sulfide, the salt is not precipitated completely unless the hydrogen ion concentration is rather low. Allen, Crenshaw, and Merwin [3] found, however, that precipitation takes place on long standing from solutions which are quite strongly acid. Some data represented graphically in Fig. 41 show that precipitation is complete in 10 days or less from 0 3 *N* H_2SO_4 and is 98.5% complete from 0.4 *N* H_2SO_4. The time interval before precipitation starts increases with increasing concentration of acid. In spite of the slowness with which the precipitate forms, the product is

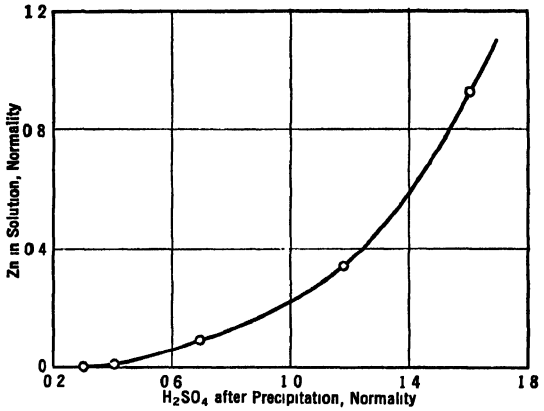


FIG 41.—Influence of free acid on the precipitation of zinc sulfide.

always a gel containing no microscopically visible crystals; on the other hand, the gel obtained by slow precipitation or by aging contains much larger particles than a fresh, rapidly formed gel and is much less soluble.[4]

In analytical practice the best hydrogen ion concentration for complete precipitation is between approximately pH = 2 and pH = 3.[5] At much lower pH values the precipitation is too slow or is incomplete, and at values higher than pH = 3 the precipitation is so rapid

[3] Am. J. Sci., (4) **34**, 355 (1912); Glixelli: Z. anorg. Chem., **55**, 297 (1907); Kolthoff and van Dijk: Pharm. Weekblad, **59**, 1351 (1922).

[4] Bruner and Zawadzki: Bull. acad. sci. Krakow, 296 (1909); Z. anorg. Chem., **65**, 136 (1910); Bruni and Padoa: Atti accad. Lincei, (5) **14** II, 525 (1905); Glixelli: Z. anorg. Chem., **55**, 297 (1907); Krokowski: Roczniki Chem., **13**, 561 (1933); Kolthoff and Moltzau: Chem. Rev., **17**, 293 (1935).

[5] Fales and Ware: J. Am. Chem. Soc., **41**, 488 (1919).

that the slimy gel produced is very difficult to filter. Higher acid concentrations can be used, of course, provided that the hydrogen sulfide pressure is increased.[6] Quantitative precipitation is usually carried out in solutions of acetic acid (containing sodium acetate),[7] tartaric acid,[8] formic acid,[9] thiocyanic acid,[10] or dilute mineral acids. The precipitates are frequently so gelatinous that filtration is difficult or slow. Jeffreys and Swift[11] obtained a dense granular mass by precipitation at 60 to 90° at a *p*H value of 1.6 maintained by a sulfate-acid sulfate buffer; the precipitation was quantitative in 25 to 40 minutes. Similarly, Mayr[12] obtained a granular precipitate by carrying out the process in a chloroacetic acid-acetate buffer at a *p*H value of 2.6. Schilling[13] claims to get a more granular precipitate from a solution containing benzene sulfonic acid.

Zinc sulfide is carried down from strongly acid solution by the second group sulfides, copper (p. 236), mercury (p. 262), bismuth, lead,[14] and tin.[14] Kolthoff claims that this phenomenon is the result of post-precipitation with the first three salts (*cf.* p. 256). Similarly zinc sulfide is contaminated by the sulfides of manganese, cobalt, nickel, and iron,[15] when precipitated in their presence. It is an open question to what extent these examples of "induced" precipitation are post-precipitation effects and to what extent they result from coprecipitation or mixed crystal formation. Schnasse[16] who worked with manganese and zinc mixtures obtained evidence from x-ray analysis which indicated mixed crystal formation. Under the conditions of precipitation employed, a miscibility gap was indicated between 20 and 84 atomic per cent of manganese; precipitates with compositions corresponding to the gap were found to consist of two separate phases. In any event, the contamination may be reduced to a minimum in actual

[6] Bruni and Padoa: Atti accad Lincei, (5) **14** II, 525 (1905)

[7] Villiers: Compt. rend., **108**, 236 (1889).

[8] Alt and Schulze: Ber, **22**, 3259 (1889).

[9] Fales and Ware: J. Am. Chem. Soc, **41**, 487 (1919).

[10] Zimmermann: Ann, **199**, 1 (1819).

[11] J. Am. Chem. Soc, **54**, 3219 (1933).

[12] Z. anal. Chem., **92**, 166 (1933); **96**, 273 (1934); *cf* Frers: **95**, 1, 113, 138 (1933).

[13] Chem-Ztg., **36**, 1352 (1912).

[14] Lassieur: Chimie & industrie, special No. 153 (1932).

[15] Funk: Z. anal. Chem., **46**, 93 (1907); *cf* Kato: J. Chem. Soc Japan, **54**, 867 (1933); **55**, 293, 1148 (1934); Kling, Lassieur, and Lassieur: Compt rend., **180**, 517 (1925); Ruff: Z. anorg Chem., **185**, 387 (1930).

[16] Schnasse: Z. physik. Chem., **B20**, 89 (1933).

analytical procedures by a suitable adjustment of the concentration, temperature, and *p*H of the solution to be analyzed.

A zinc sulfide gel is obtained by the action of sodium thiosulfate on a solution of zinc salt in the cold or at 100°,[2] and by the alternating-current electrolysis of sodium thiosulfate solution with zinc electrodes.[17] It is also formed by direct-current electrolysis of an ammonium chloride solution using a zinc cathode and an anode of zinc coated with sulfur.[18] Liesegang rings of both zinc and cadmium sulfides can be formed by precipitation in gelatin or agar jelly.[19]

The freshly formed gel of zinc sulfide contains a great deal of adsorbed water. If dried under suitable conditions, compositions corresponding to hydrates such as $2ZnS \cdot H_2O$, $3ZnS \cdot H_2O$, $4ZnS \cdot H_2O$, $3ZnS\ 2H_2O$, and $ZnS \cdot H_2O$ can be obtained; but it is probable that each one is merely a hydrous sulfide whose composition is the accidental result of the conditions of drying.

Owing to the solubility of zinc sulfide in acid solution, fibers impregnated with the salt may be employed in the microchemical detection of a number of metals which give colored sulfides.[20] Chamot and Cole[21] dipped swollen wool fibers alternately in zinc acetate, which is fairly strongly adsorbed by the fibers, and sodium sulfide, thereby obtaining fibers which are sensitive to 0.001 mg of copper. To make the test, a drop of the unknown solution is placed on an object glass and acidified with a drop of dilute hydrochloric acid; in the drop is placed a small piece of the impregnated wool fiber which is subsequently examined under the microscope for color change.

Zinc sulfide is a valued white pigment, both alone and when mixed with barium sulfate to give the commercial product known as lithopone The properties and application of zinc sulfide pigments will be considered in a later chapter (p. 281).

Zinc Sulfide Sol

A gel of zinc sulfide freshly formed in the cold is easily peptized by removing the adsorbed salts by washing.[22] Even when precipitated

[17] Le Blanc and Schick: Z. physik. Chem., **46**, 213 (1903).

[18] Griffith: Ger. Pat 332,199 (1921); Gmelin: "Handbuch anorg. Chem.," (8) **32**, 196 (1924); *cf., also,* Jacolliot: French Pat 415,605 (1910); Chem. Abstracts, **6**, 1884 (1912).

[19] Daus and Tower: J. Phys. Chem., **33**, 605 (1929).

[20] Emich and Donau: Ann, **351**, 432 (1907).

[21] Ind. Eng. Chem, **10**, 48 (1918).

[22] Donnini: Gazz. chim. ital., **24** I, 219 (1894).

hot and allowed to stand several hours, the quantitative analyst must have ammonium sulfide or ammonium chloride in the wash water to prevent sol formation. For obtaining more concentrated sols, the gel is thrown down from an ammoniacal solution with hydrogen sulfide, washed by decantation, and suspended in water through which hydrogen sulfide is passed until peptization is complete.[23] This procedure may be modified by suspending freshly precipitated hydrous zinc oxide in water into which hydrogen sulfide is conducted until the oxide is completely transformed into an opalescent zinc sulfide sol. The excess hydrogen sulfide may be removed by heating to boiling, but prolonged heating decreases the stability and may cause precipitation. In the latter event, repeptization can be effected by treating with hydrogen sulfide, but the process requires more time with the aged gel than with a freshly formed one.[24] The peptizing action of hydrogen sulfide increases with the pressure up to 1.5 to 2 atmospheres, above which it apparently decreases slightly.[25]

A pale opalescent sol is formed by the action of NaHS on a dilute solution of zinc sulfate.[26] Muller [27] was unsuccessful in an attempt to prepare a stable sol by the interaction of ammonium sulfide and zinc sulfate in the presence of a large amount of glycerol; the increased viscosity slows down the agglomeration, but the sulfide settles out after a few days. The stability of the sol is increased enormously if prepared in the presence of protecting colloids, such as gum arabic [28] and gelatin.[29]

A dilute sol appears clear in transmitted light, and a concentrated sol possesses an orange-red color and shows a bluish fluorescence. The gel which precipitates from the sol either spontaneously or by the action of electrolytes is not a hydrosulfide such as $7ZnS \cdot H_2S$ or $12ZnS \cdot H_2S$ [30] but is zinc sulfide with adsorbed hydrogen sulfide, the stabilizing electrolyte in the sol.

[23] Winssinger: Bull. soc chim., (2) **49**, 452 (1888).
[24] Villiers: Compt. rend., **120**, 149, 188 (1895).
[25] Young and Goddard: J. Phys. Chem., **21**, 1 (1917).
[26] Thomsen: Ber., **11**, 2044 (1878); von Zotta · Monatsh, **10**, 807 (1889)
[27] Chem.-Ztg., **28**, 357 (1904).
[28] Lefort and Thibault: J. pharm. chim., (5) **6**, 169 (1882).
[29] Alexander: U. S. Pat. 1,259,708 (1918).
[30] Linder and Picton: J. Chem. Soc., **61**, 114 (1892).

COLLOIDAL CADMIUM SULFIDE

The Precipitated Salt

A highly hydrous gel of cadmium sulfide is precipitated by the action of hydrogen sulfide or alkali sulfides on a cold solution of cadmium salt. The tendency to crystallize is more marked with cadmium sulfide than with the corresponding zinc salt; hence the gel formed at room temperature gives fairly sharp x-ray interference rings.[31] Microscopic crystals result by precipitation or digestion at higher temperatures. A gel precipitated from a solution containing 2 g $CdSO_4$ in 20 cc of 30% H_2SO_4 gave crystals 0.5 mm long, identical with the mineral greenockite, after digestion in the mother liquor for 3 days at 180°.[32] Similarly, a gel digested at 150 to 200° with ammonium sulfide which has a slight solvent action gave large crystals similar to greenockite.[33]

In the absence of x-ray diffraction methods of examination, Allen, Crenshaw, and Merwin were unable to determine the structure of the extremely minute crystals of the freshly precipitated salt and were forced to grow them to a size that could be observed optically, either by heating the dry powder or by digesting the mass under pressure at high temperatures. This always yielded hexagonal crystals like greenockite; but Böhm and Niclassen [34] showed by x-ray diffraction methods that the yellow precipitate thrown down from cadmium sulfate solution was cubic, being similar to cubic zinc blende. This was confirmed by Ulrich and Zachariasen,[35] who showed that cubic or β-CdS ($a_0 = 5.820$ Å) was precipitated from a saturated cadmium sulfate solution by hydrogen sulfide; on heating this yellow cubic sulfide to 700–800° in the presence of sulfur vapor, hexagonal or α-CdS resulted.

Milligan [36] in the author's laboratory confirmed and extended these observations (p. 295). Cubic or β-CdS chiefly was obtained from hot solutions of cadmium sulfate and from both hot and cold solutions of acidified sulfate and nitrate. On the other hand, hexagonal or α-CdS was thrown down chiefly from cadmium chloride, bromide, and iodide,

[31] Haber: Ber., **55B**, 1730 (1922).

[32] Allen, Crenshaw, and Merwin: Am. J. Sci, (4) **34**, 362 (1912); *cf.* Baubigny: Compt. rend., **142**, 577 (1906).

[33] Stanek: Z. anorg. Chem., **17**, 117 (1898).

[34] Z. anorg. Chem., **132**, 1 (1924).

[35] Z. Krist., **62**, 260 (1925).

[36] Milligan: J. Phys. Chem., **38**, 797 (1934).

both hot and cold and with and without the presence of the corresponding acid.

For complete precipitation of cadmium sulfide, the solution must be saturated with hydrogen sulfide since prolonged action of acids, even in the cold, dissolves appreciable amounts of the salt.[37] The equilibrium constant of the reaction $CdSO_4 + H_2S \rightleftarrows CdS + H_2SO_4$ from solubility determinations in approximately M H_2SO_4 containing a very little H_2S is: $k = 6.6 \times 10^{-6}$ for the sulfide from $CdCl_2$ and 4.6×10^{-7} for the sulfide from $CdSO_4$. Approaching the equilibrium from the left by precipitation studies, the constant is $k = 16 \times 10^{-6}$.[38] The variation from a constant value is the result of differences both in particle size and in crystal structure.

A gel of cadmium sulfide is also obtained by the action of sodium thiosulfate on a solution of cadmium salt at the boiling point;[39] by the electrolysis of a solution of sodium thiosulfate containing a little sodium chloride, with a cadmium anode and an indifferent cathode; and by the alternating-current electrolysis of 10% $Na_2S_2O_3$ solution with cadmium electrodes.[40] A more satisfactory electrolytic method appears to be the electrolysis of a sodium sulfate solution with a cadmium anode and a cathode consisting of a mixture of copper sulfide and sulfur.[41] The electrolytic methods have been suggested for the technical formation of cadmium yellow and will be referred to again in the chapter on the sulfide pigments.

Purity: Adsorption of Chloride. Precipitated cadmium sulfide is always contaminated by anions in the solution from which it separates. The determination of cadmium as sulfide, especially in the presence of sufficient hydrochloric acid to ensure its separation from zinc, has long been regarded as a useless method because of the chloride carried down with the precipitate. Treadwell[42] attributes the contamination to the formation of a double salt, $CdS\ CdCl_2$, in varying amounts depending on the acid concentration and the temperature and pressure at which the precipitation is carried out. Egerton and Raleigh[43] believe the precipitate to have a constant composition when

[37] Stull: J Am. Chem Soc, **23**, 512 (1901); Bruni and Padoa: Atti accad. Lincei, (5) **14** II, 525 (1905).

[38] Bruner and Zawadzki: Bull acad sci. Krakow, 296 (1909).

[39] Donath: Z. anal. Chem, **40**, 141 (1901).

[40] Richards: Trans. Am Electrochem. Soc., **1**, 221 (1902).

[41] Lorenz: Z anorg. Chem, **12**, 442 (1896); Bernfeld: Z. physik. Chem., **25**, 46 (1898).

[42] Treadwell-Hall: "Analytical Chemistry," **2**, 191 (1912); *cf., also,* Hulot: Bull. soc. chim., (4) **41**, 313 (1927).

[43] J. Chem. Soc., **123**, 3019 (1923).

thrown down at 80° from a solution containing 4 cc of concentrated HCl in 100 cc, and washed with an unspecified, definite quantity of water. Under these conditions, the precipitate is said to contain 8.16% of the alleged salt, $CdS \cdot CdCl_2$; hence, in determining cadmium quantitatively by weighing the sulfide, the molecular weight of the precipitate is taken to be 147.4 instead of 144.47 for pure cadmium sulfide.

Since conclusive evidence of the existence of a definite double salt $CdS\ CdCl_2$ is lacking, Weiser and Durham [44] suggested that the contamination of the sulfide gel is due to adsorption of cadmium chloride in varying amounts depending on the conditions. To test this hypothesis, hydrogen sulfide at room temperature was passed into a definite volume of solution containing a constant amount of cadmium chloride and varying amounts of hydrochloric acid. The precipitate was fil-

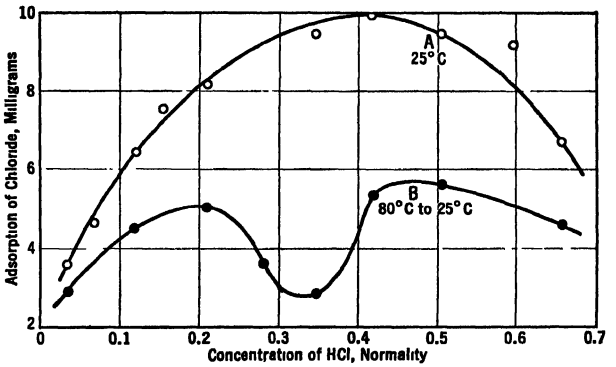


FIG 42.—Adsorption of chloride by cadmium sulfide.

tered on a Gooch crucible, washed until the wash water gave no test for chloride, and then analyzed for the chloride content. The results are shown graphically in curve *A* of Fig. 42. The filtrates were tested for completeness of precipitation by rendering them alkaline with ammonia and saturating with hydrogen sulfide. With the most acid solution a faint yellow coloration was noted but no precipitate. The amount of cadmium required to produce this coloration was found to be negligible as compared with the total amount of precipitate.

An attempt was made to repeat the above observations at 80° as recommended by Egerton and Raleigh, but precipitation was found to be far from complete. Accordingly, the several solutions were

[44] J. Phys. Chem., **32**, 1061 (1928).

heated to 80°, removed from the source of heat, and hydrogen sulfide conducted through continuously while they cooled down to room temperature. The precipitates were washed and analyzed for chloride with the results shown graphically in curve *B* of Fig. 42.

Referring to curve *A*, it will be seen that the amount of chlorine in the precipitate does not increase continuously with the concentration of hydrochloric acid but exhibits a maximum. This maximum corresponds to a visible change in the physical character of the precipitate from a flocculent to a distinctly granular structure. The curve is thus a typical adsorption curve showing a maximum that results from a physical change in the adsorbent.

Curve *B* for the second series of experiments lies under curve *A*, as would be expected since the temperature at which the precipitation starts is higher, hence the precipitate is more granular and the adsorption is less. With increasing concentration of acid, the adsorption of chloride increases so that the first part of curve *B* is very similar to that of curve *A*, and for the same reason. But when the acid reaches a concentration in the neighborhood of 0.3 *N* the amount of cadmium sulfide precipitated in the hot decreases with a corresponding increase in the amount precipitated at lower temperatures. This means a larger amount of finely divided particles and a correspondingly greater adsorption which rises to a second maximum. This behavior would be difficult to explain on the basis of double salt formation but is readily accounted for by considering the contamination as a case of adsorption. The final concentration of acid recommended by Egerton and Raleigh was approximately 0.5 *N*. This might appear to account for the constancy of composition of their precipitates since curve *B* is relatively flat when the HCl concentration is in the neighborhood of 0.5 *N*. However, the chlorine content under these conditions corresponds to 12.2% of the alleged double salt instead of to 16.5% as calculated from Egerton and Raleigh's results; the difference is, of course, in the conditions of the precipitation.

Precipitated cadmium sulfide may carry down with it the sulfides of other elements. Evidence from x-ray analysis indicates that the coprecipitation effect with mercury [45] and manganese [46] results from mixed crystal formation.

Color. In general, the color of cadmium sulfide gel is light yellow when thrown down from cold solutions of low cadmium content by

[45] Bottger and Druschke: Ann., **453**, 315 (1927); Ahrens: Dissertation, Leipzig (1933); Kolthoff and Moltzau: Chem. Rev., **17**, 293 (1935).

[46] Schnasse: Z. physik. Chem., **B20**, 89 (1933).

hydrogen sulfide or by alkali sulfides, whereas the color is a deep orange when precipitated from hot acid cadmium solutions with hydrogen sulfide or by boiling cadmium solutions with an excess of sodium thiosulfate. Microscopic crystals likewise vary in color from clear yellow to orange. Because of the importance of cadmium sulfide as a pigment,[47] the factors influencing the color will be considered in some detail in the chapter on the sulfide pigments (p. 295).

Cadmium Sulfide Sol

Preparation. A sol of cadmium sulfide is best prepared by precipitating an ammoniacal solution of cadmium sulfate or cadmium chloride[48] with hydrogen sulfide, washing the precipitate by decantation, and suspending in water through which hydrogen sulfide is conducted until peptization is complete. The excess hydrogen sulfide can be removed by boiling.

Sols may be obtained directly by conducting hydrogen sulfide into 0.0004 *N* $CdSO_4$[49] or 0.025 *N* $Cd(C_2H_3O_2)_2$.[50] The stability of the preparations may be increased greatly by the presence of casein, gum arabic,[51] soaps,[52] and probably by sugar,[53] which is adsorbed by the colloidal particles.

A benzine sol of cadmium sulfide may be prepared by triturating the gel with heavy oil and shaking the mixture with the light petroleum distillate.[54] Oleates may be used as protecting colloids in the preparation of zinc and cadmium sulfide sols in benzene, toluene, and linseed oil.[55]

Properties. The sol prepared by Prost's method is a beautiful golden yellow in transmitted light and is somewhat fluorescent in reflected light. Dilute sols are quite stable for a considerable time, but a preparation containing as much as 11 g/l precipitates in 24 hours. As in all sulfide sols, the particles are negatively charged owing to preferential adsorption of S^{--} and HS^{-} ions. The ratios of the precipi-

[47] *See* Bugden: Continental Met. & Chem. Eng., **2**, 109 (1927).

[48] Prost: Bull. acad roy. méd. Belg., (3) **14**, 312 (1887); J. Chem. Soc., **54**, 653 (1888).

[49] Meldrum: Chem. News, **79**, 170 (1899); Vanino and Hartl: Ber, **37**, 3622 (1904).

[50] Bialek: Roczniki Chem., **14**, 1499 (1934).

[51] Muller and Artmann: Oesterr. Chem.-Ztg., **7**, 149 (1904).

[52] Bhatnagar, Prasad, and Bahl: J. Indian Chem. Soc., **2**, 11 (1925).

[53] Prasad, Shrivastava, and Gupta: Kolloid-Z., **37**, 101 (1925).

[54] Van Dorp and Rodenburg: Chem. Weekblad, **6**, 1038 (1909).

[55] Bechhold and Szidon: Kolloid-Z. (Zsigmondy Festschrift), **36**, 259 (1925).

tating powers of the sulfates of potassium, aluminum, and cadmium are 1 : 140 : 150. The high precipitating power of cadmium salts doubtless results from the removal of the stabilizing electrolyte, hydrogen sulfide. Plant and animal fibers are colored by colloidal cadmium sulfide; but in this form the color is not adsorbed sufficiently strongly to serve as a dye.

Bialek[50] followed the coagulation of cadmium sulfide sol with a spectrophotometer, and found that the process could be represented by the equation $K(t - t_s) = \ln (x/1 - x)$, where K is the velocity constant; x, the relative degree of turbidity; t, the time; and t_s, the half-time period of coagulation. The process was autocatalytic, larger particles hastening the coagulation of smaller ones. The coagulating powers of several cations followed the usual order: $Li < Na < K < NH_4 < Rb < Cs$; $Ca < Sr < Ba$.

A study of the viscosity and rigidity of copper ferrocyanide and cadmium sulfide sols[56] disclosed that some sols possess true rigidity, that is, they support small stresses permanently without yielding. The sols were found to exhibit a linear relationship between stress and strain, behaving like perfectly elastic bodies under the experimental conditions.

COLLOIDAL MERCURIC SULFIDE

The Precipitated Salt

Formation. Black mercuric sulfide is thrown down in a hydrous form by the action of excess hydrogen sulfide on a mercuric salt in an acid or neutral solution. Even when freshly precipitated at 0°, the sulfide gives an x-radiogram which shows that the crystals possess the cubic structure similar to zinc blende and identical with the mineral meta-cinnabarite.

Black mercuric sulfide is also obtained by the action of mercuric chloride on a solution of sodium thiosulfate at concentrations in which the ratio of mercuric chloride to sodium thiosulfate lies between 2 : 3 and 1 : 4; at higher thiosulfate concentrations, red mercuric sulfide is precipitated.[2] The black gel is formed by the alternating-current electrolysis of hot sodium thiosulfate solution with mercury electrodes.[57] Since the alternating current causes the mercury to vibrate, the surface of the mercury is kept free from precipitated sulfide; hence, the current efficiency is much higher than obtains in the alternating-current

[56] McDowell and Usher: Proc. Roy. Soc. (London), **131A**, 409 (1931)
[57] Weiser: J Phys. Chem., **22**, 77 (1918).

electrolysis with zinc and cadmium electrodes under similar conditions. Moreover, the mercury electrodes are uniform and the experimental conditions are therefore reproducible. In Fig 43 the current efficiency at varying concentrations of electrolyte and at varying current densities is shown for a 60-cycle alternating current. The marked falling off in the efficiency with thiosulfate solutions stronger than 35% is due to the rapid action of the hot electrolyte on the mercury, forming a film which prevents the rhythmical pulsations of the surface.

Red mercuric sulfide or cinnabar is the stable modification at all temperatures up to its sublimation point, about 580°. It is formed

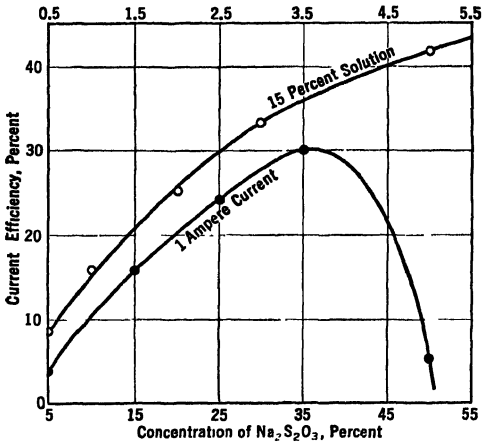


FIG 43.—Efficiency of the electrolysis of sodium thiosulfate solutions at mercury electrodes with a 60-cycle alternating current.

from the black gel by digesting the gel with alkali or ammonium sulfide. The process consists in the solution of the black regular form and the subsequent precipitation of the less soluble red hexagonal modification. The red sulfide precipitates directly when Hg(SH)CNS is boiled with concentrated NH_4CNS or when hydrogen sulfide is conducted into a warm mercuric salt solution in the presence of acetic acid and excess NH_4CNS or $CS(NH_2)_2$.[58] The interaction of mercuric chloride and concentrated sodium thiosulfate gives a red sulfide which Allen, Crenshaw, and Merwin took to be a third allotropic modification; but x-radiograms proved it to be identical with cinna-

[58] Venkataramaiah and Rao. J. Sci. Assoc. Maharajah's Coll, **1**, 41 (1923); Chem. Abstracts, **18**, 626 (1924); *cf.* Alvisi: Atti accad. Lincei, (5) **7** II, 97 (1898).

bar.[59] When properly prepared, red mercuric sulfide furnishes a valuable red pigment known as vermilion (p. 297).

Contamination. When mercuric chloride is precipitated with hydrogen sulfide or alkali sulfide, the precipitate may be first white, then yellow, and finally black. The white precipitate is $2HgS \cdot HgCl_2$, the black is HgS, and the yellow, a mixture of the two.[60] If a small excess of sodium sulfide is used as precipitant, a sol is formed which is yellow at first and then changes to black.[61] In the precipitation of alkali halides (X = Cl, Br, or I), Smith and Semon [62] suggest that five consecutive reactions take place with the formation of four intermediate compounds: $[Hg(SH)_2Hg]X_2$, $[HgSHHg]X_2$, $[Hg(SHg)_2]X_2$, and $[Hg(SHg)_2]SH_2$. Fenimore and Wagner [63] believe that the high results which they obtain in the estimation of mercury as sulfide may result from the incomplete conversion of the alleged intermediate compounds into HgS. It will be recalled that Weiser and Durham attributed the contamination of cadmium sulfide with chloride to adsorption.

Mercuric sulfide is contaminated by third-group sulfides when precipitated in their presence even when the acidity is such that mercuric sulfide alone would be expected to precipitate. Moreover, a cadmium solution so strongly acid that no precipitate results with hydrogen sulfide will precipitate a great deal of cadmium on the addition of a mercury solution. The explanations that have been advanced to account for the induced precipitation have already been given (p. 252). The contamination of mercuric sulfide by zinc has received special consideration by Kolthoff,[64] who attributes the phenomenon to post-precipitation. Freshly precipitated mercuric sulfide on which zinc sulfide is post-precipitated is quite as black as the pure compound, but it is much more slimy and difficult to filter. Aging of the black sulfide cuts down its tendency to promote the precipitation of zinc. A certain "aged" condition is reached more quickly at higher than at lower temperatures, possibly because of an increased tendency toward transformation to the cinnabar structure at higher temperatures. The same explanation doubtless accounts for the greater promoting action of the sulfide aged in acid solutions.

[59] Kolkmeijer, Bijvoet, and Karssen: Rec. trav. chim., **43**, 894 (1924).

[60] Jolibois and Bouvier: Compt. rend., **170**, 1497 (1920).

[61] Morosow: Kolloid-Z., **36**, 21 (1925).

[62] J. Am. Chem. Soc., **46**, 1325 (1924).

[63] J. Am. Chem. Soc., **53**, 2453 (1931).

[64] Chem. Weekblad, **31**, 102 (1934); Kolthoff and Molzau: Chem. Rev., **17**, 293 (1935); J. Phys. Chem., **40**, 779 (1936).

At higher acidities, the amount of zinc sulfide entering a mercuric sulfide precipitate in a given time falls off much more slowly with increasing acidities than would be expected from solubility relations. With freshly precipitated mercuric sulfide and a certain degree of acidity, an appreciable quantity of zinc enters the solid phase within the first 30 minutes or so after saturating with hydrogen sulfide, after which the precipitation takes place more slowly to a point corresponding to the solubility of well-aged zinc sulfide. At lower acidities the presence of a very small amount of mercuric sulfide will lead to the precipitation of relatively large amounts of zinc sulfide within a period of time such that no precipitate would result from a solution of zinc salt alone; at higher acidities (2 N H_2SO_4), the amount of zinc sulfide entering the precipitate in a given short time of shaking is approximately proportional to the amount of fresh mercuric sulfide present. Keeping the acidity and the amount of mercuric sulfide constant, the amount of zinc carried down is approximately proportional to the amount of zinc salt in solution over a limited range.

Kolthoff attributes the results above described to (1) adsorption phenomena and (2) true precipitation, in varying degrees depending on the acidity. During the initial period, adsorption is the primary process at both high and low acidities; and at high acidities, where the rate of true precipitation is very slow, adsorption phenomena are likewise responsible for the contamination. The mechanism is as follows: mercuric sulfide adsorbs sulfide ions primarily with hydrogen ions the counter ions in the double layer; zinc ions in contact with the sulfide enter into exchange adsorption with hydrogen ions thus contaminating the precipitate with zinc sulfide. The presence of strychnine and aluminum ions which will undergo the same exchange adsorption phenomena will cut down the adsorption of zinc ions. Hydrogen ions in high concentration will likewise cut down greatly the adsorption of zinc ions by exchange. This accounts both for the smaller adsorption of zinc at high acidities and for the fact that the contamination is approximately proportional to the zinc ion concentration at high acidities.

Mercuric Sulfide Sols

Preparation. The hydrosol of mercuric sulfide is easily prepared by washing the black loose precipitate with water and suspending in water through which a rapid current of hydrogen sulfide is passed.[33,65] If the gel has aged until it possesses a metallic appearance with a

[65] Freundlich and Schucht: Z. physik. Chem., **85**, 641 (1913).

grayish tinge, peptization is accomplished with difficulty if at all. Excess hydrogen sulfide may be removed by boiling, but it is better to wash with hydrogen. The concentrated sol is deep black whereas the dilute sol is brown with a greenish fluorescence in reflected light.

A sol results on conducting hydrogen sulfide into a cold saturated solution of mercuric cyanide.[66] Owing to low ionization of hydrocyanic acid, it has only a slight precipitating action; but the sol is more stable when the impurity is removed, preferably by distillation under reduced pressure in an atmosphere of hydrogen sulfide. An alcosol can be prepared in a similar way by conducting dry hydrogen sulfide into an alcoholic solution of mercuric cyanide[67] and dialyzing against pure alcohol, using membranes of parchment or collodion.[68] Weiser and Mack[69] obtained sols in methyl, ethyl, and *n*-propyl alcohols and in acetone by suitable modifications of this procedure.

Lottermoser[70] prepared a hydrosol by adding sodium sulfide dropwise to 1 cc of saturated mercuric chloride until the precipitate just redissolved and pouring the resulting solution of alkali mercurisulfide into 1 l of distilled water. It is also formed by the action of the silent electric discharge on a suspension of mercuric sulfide (p. 7).

The sodium salts of lysalbinic and protalbinic acids may be used as protecting colloids in preparing a stable sol for medicinal purposes.[71] When injected intravenously, the sol is quite rapidly coagulated and becomes attached to the tissues. If the injection is subcutaneous, the sulfide remains in the subcutaneous tissue; but if it is injected intravenously, the salt appears in the liver, spleen, bone marrow, and lungs, from which it is absorbed slowly. Its administration is said to facilitate the healing of syphilitic lesions,[72] but it is not a substitute for arsenicals.[73]

Coagulation and Adsorption. The adsorption of cations during the precipitation of negative mercuric sulfide[74] is less than with the more hydrous arsenic trisulfide sol. Freundlich and Schucht[65] determined

[66] Lottermoser: J. prakt. Chem., (2) **75**, 293 (1907).

[67] Errera: Kolloid-Z., **32**, 240 (1923); *cf.* Volkov and Glazman: Chem. Abstracts, **30**, 5483 (1936).

[68] Ostwald and Wolski: Kolloid-Z., **28**, 228 (1921).

[69] J. Phys. Chem., **34**, 86, 101 (1930).

[70] Kolloid-Z., **66**, 188 (1934); Lottermoser and Hessling: **75**, 184 (1936).

[71] Wolvekamp: Brit. Pat. 188,772 (1921).

[72] Quattrini: Chem. Abstracts, **10**, 640 (1916); Sabbatani: **11**, 1206 (1917).

[73] Gennerich: Am. J. Syphilis, **16**, 198 (1932).

[74] Kruyt and van der Willigen: Z. physik. Chem., **130**, 170 (1927); (*cf. this volume*, p. 203).

the precipitation values for a number of salts and the adsorption of cations at the precipitation value in an attempt to show that equivalent amounts of all cations are adsorbed at this concentration; but since the adsorption values vary all the way from 0.004 to 0.050 m.eq./g (Table XXXIV), the results disprove the assumption. The precipita-

TABLE XXXIV

ADSORPTION OF CATIONS DURING THE PRECIPITATION OF MERCURIC SULFIDE SOLS

Cation	Adsorption at precipitation value, milliequivalent	Precipitation value, millimols	Concentration of colloid, grams per liter
NH_4	0 050	10 20	13 74
Ag	0 020	0 28	11 74
New magenta	0 008	0 097	13 74
Brilliant green	0 004	0 048	8 38
Auramine	0 011	0 094	10 05
Methylene blue	0 007	0 097	14 96
Ba	0 044	0 510	8 29
$Cu[Cu(NO_3)_2]$	0 030	0 150	8 26
$Cu(CuSO_4)$.	0 022	0 260	14 43
Ce	0 012	0 082	10 45

tion values of new magenta and methylene blue are identical, and the adsorption values are almost the same; on the other hand, the precipitation value of auramine is but 3% lower than that of new magenta, and the adsorption value is 37% higher. Moreover, the precipitation value of brilliant green is only one-half that of new magenta, and the adsorption value at this concentration is but half as much instead of being the same or larger in accord with Freundlich's conclusions from experiments on the adsorption of organic cations by arsenic trisulfide. There is no doubt that the anion has some effect, but this cannot account for the precipitation value of cupric sulfate being 75% higher than for cupric nitrate and the adsorption of copper from nitrate solution being 25% greater than from sulfate solution.

The cause of the variation from equivalent adsorption has been considered in some detail in an earlier chapter (p. 204); but no mention was made of the much greater variation with mercuric sulfide than with arsenic trisulfide. When mercuric sulfide sol is first flocculated it is quite gelatinous but it becomes granular rapidly and gives up a part of the adsorbed electrolyte. It is altogether probable that the

physical character of the precipitated sulfide varies appreciably with different electrolytes, thus accounting for the greater variation from equivalent adsorption by mercuric sulfide than by arsenic trisulfide.

Reversal of Adsorption. The course of the adsorption reversal of mercuric sulfide has been followed by Freundlich.[75] Portions of 250 cc each of a sol were treated with 25 cc of auramine of varying concentrations. The mixtures were stirred continuously, and at intervals samples were withdrawn, freed from suspended sulfide, and analyzed colorimetrically. The S-shaped form of the time-desorption curves indicates that the adsorption reversal and, hence, the coarsening of the particles are autocatalytic processes. Furthermore, the velocity of the processes rises rapidly with increasing concentration of the coagulating dye. The mechanism is about as follows: When sufficient electrolyte is added to a sol, the charge on the colloidal particles is reduced below the critical value necessary for agglomeration. If the electrolyte concentration is near the precipitation value, the primary particles of the flocs still possess a slight charge which tends to keep them from coalescing; but with crystalline particles which are not very hydrous, like those of mercuric sulfide, the low residual charge is not sufficient to prevent a gradual coalescence and packing together of the particles, thereby giving a diminished surface and a lessened adsorption. The rate of coalescence increases with diminishing residual charge and hence is greater the higher the concentration of precipitating electrolyte up to the point where charge reversal would come in. The apparent autocatalytic course may be the result of two processes: a slow initial formation of secondary aggregates from primary particles and a more rapid packing together of the larger aggregates.

[75] Freundlich and Schucht: Z. physik. Chem., **85**, 660 (1913); Freundlich and Hase. **89**, 417 (1915).

CHAPTER XIV

THE COLLOIDAL SULFIDES OF MANGANESE, NICKEL, COBALT, IRON, AND THE RARER ELEMENTS

COLLOIDAL MANGANOUS SULFIDE

Ammonium sulfide and monosulfides of the alkali metals precipitate from a solution of manganous salt, a rose or flesh-colored gel of manganous sulfide which oxidizes readily in the air, assuming a brown tint.[1] The precipitation is very slow or incomplete from dilute solutions unless a salt such as ammonium chloride is present.[1] It is probable that this salt acts by preventing sol formation. Citrates and tartrates prevent the precipitation of manganous sulfide by ammonium sulfide, and citrates stop the precipitation by alkali sulfides as well.[2] It is altogether likely that these strongly adsorbed anions act by forming a stable negative sol.

The rose-colored sulfide appears to be the stable form when precipitated with alkali sulfides; but when thrown down with ammonium sulfides it frequently assumes a green color. Conditions favorable for the transformation have been stated by a number of people.[3] The various methods have been analyzed critically by Mickwitz and Landesen.[4] As a result of this analysis and some observations of their own the following conclusions were reached: (1) The transformation from rose to green manganous sulfide never takes place when the precipita-

[1] Joulin: Ann. chim. phys., (4) **30**, 275 (1873).

[2] How: Chem. News, **19**, 137 (1869).

[3] Fresenius: J. prakt Chem., **82**, 267 (1861); Muck: Z. Chem., **12**, 580, 629 (1869); Classen: Z. anal. Chem., **8**, 370 (1869); **16**, 319 (1877); DeClermont and Guiot. Bull. soc. chim., (2) **27**, 353 (1877); Meineke: Z. angew. Chem., **1**, 4 (1888); Mourlot: Compt. rend., **121**, 202 (1895); Raab and Wessley: Z. anal. Chem., **42**, 433 (1903); Olsen, Clowes, and Weidmann: J. Am. Chem. Soc., **26**, 1622; Olsen and Rapelje: 1615 (1904); Villiers: Compt. rend, **159**, 67 (1914); Fisher: J. Russ. Phys.-Chem. Soc., **46**, 1481 (1914); Seeligmann: Z. anal. Chem., **53**, 594 (1914); **54**, 104 (1915); Hahn: Z. anorg. Chem., **121**, 209 (1922).

[4] Z. anorg. Chem., **131**, 101 (1923); Landesen: **193**, 277 (1930); J. Phys. Chem., **36**, 2521 (1932).

tion is effected with alkali sulfides. (2) The transformation from rose to green manganous sulfide never takes place except in the presence of free ammonia. (3) There are two rose sulfides of manganese. One, which will not turn green, is precipitated by NH_4HS in the absence of free ammonia; its composition may be represented by the formula $H_2Mn_3S_4$ or $3MnS \cdot H_2S$. A second rose sulfide, which turns green spontaneously, is precipitated in the presence of free ammonia; its composition may be expressed by the formula $NH_4HMn_3S_4$ or $3MnS \cdot NH_4HS$. In the next section it will be shown that all three of these conclusions are open to question.

Transformation from Rose to Green Manganous Sulfide

Effect of Excess Alkali Sulfide and of Ammonia. The rose sulfide may be transformed into green in the presence of an excess of alkali

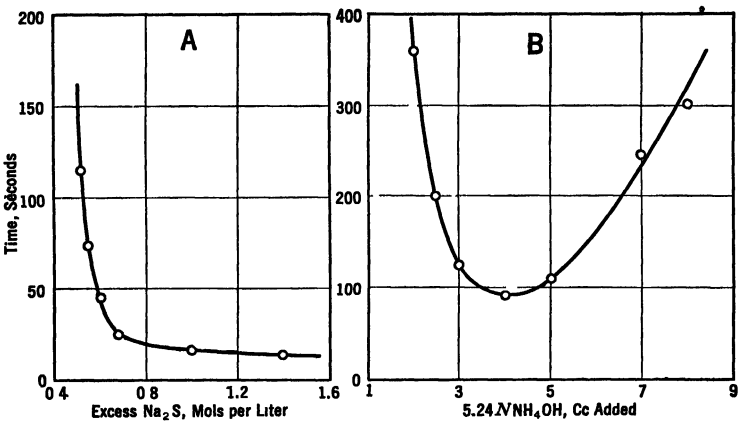


FIG 44.—Effect of the concentration of (*A*) sodium sulfide and (*B*) ammonium hydroxide on the rate of transformation from rose to green manganous sulfide.

sulfide slowly at room temperature and rapidly at the boiling point; free ammonia is not necessary for the transformation.[5] Some observations of the rate of transformation of 0.435 g of the rose sulfide to green at the boiling point, in the presence of varying amounts of sodium sulfide, are shown graphically in part *A* of Fig. 44. Under the conditions of the experiment, the rose is transformed into the green in a short time, only if the alkali sulfide concentration is greater than approximately 0.5 *M*.

[5] Weiser and Milligan: J. Phys. Chem., **35**, 2330 (1931); **36**, 2840 (1932).

In part *B* of Fig. 44 are given the results of observations similar to the above on the effect of ammonium hydroxide on the rate of transformation at room temperature of the rose sulfide precipitated by NH_4HS in slight excess (0 05 mol/l). The U-shaped curve signifies that an optimum concentration of ammonia exists which is most favorable for rapid transformation. With too little ammonia no change takes place in a reasonable time; with too much ammonia, the rate is retarded. It was found also that free ammonia has little or no effect on the transformation when but little excess NH_4HS is added. Moreover, the greater the excess of NH_4HS [$(NH_4)_2S$], the greater the amount of ammonia which must be added in order to give the critical mixture for the most rapid rate of transformation. Finally, the greater the excess of ammonia, the higher must be the concentration of NH_4HS [$(NH_4)_2S$] to inhibit or prevent the change. The more rapid the mixing, other things being equal, the more rapid the rate of transformation.[6]

A probable explanation of the above behavior is as follows: The change from the flocculent rose precipitate, consisting of aggregates of finely divided particles, to the denser green granules appears to be favored by dissolution of the rose and reprecipitation of the more insoluble[7] green form having a different crystal structure. The rose sulfide appears to be almost insoluble in an excess of NH_4HS, and, in view of the lower solubility of manganous sulfide than of manganous hydroxide, the former is probably but very slightly soluble in ammonium hydroxide. On the other hand, rose manganous sulfide is somewhat soluble in $(NH_4)_2S$.[8] Accordingly the addition of ammonium hydroxide to a given excess of NH_4HS gives an optimum concentration of $(NH_4)_2S$ which is most favorable for the transformation. With too little ammonia the change is very slow, and with too much ammonia the adsorption is sufficiently great to form a film around the particles and so to inhibit the transformation. The rate of mixing is important since it determines the form of the precipitate. The precipitate obtained by slow mixing is a fairly dense floc that is not greatly protected by adsorbed ammonia, at least when the ammonia concentration is not too high. On the other hand, rapid mixing gives a highly dispersed precipitate, the individual particles of which adsorb ammonia and are protected thereby so that the rate of change is greatly retarded.

[6] *Cf.* Fisher: J. Russ Phys.-Chem Soc, **46**, 1481 (1914).
[7] Weigel: Z physik. Chem., **58**, 294 (1907).
[8] Abegg: "Handbuch anorg Chemie," **4** (*2*), *724* (1913)

Tower [9] obtained Liesegang rings of manganese sulfate in gelatin, agar, and silica jellies. Unfortunately he does not state whether the transformation from rose to green was prevented by the hydrophilic colloid.

X-ray Analysis. X-ray analysis [5] of the light green sulfide obtained with sodium sulfide and the dark green preparation obtained with ammonium sulfide disclosed that the two are identical. The crystals of the so-called α-sulfide are cubic of the sodium chloride type; the value of the lattice constant, a_0, for the crystals is 5.20 Å.[10] The structure is identical with that of the mineral alabandite.

The rose or β-sulfide exists in two modifications, the usual hexagonal modification of the wurtzite type and a cubic modification of the zinc blende type which was overlooked by Weiser and Milligan and found by Schnaase.[10] The rose cubic form is obtained in strong alkaline solution, hence by precipitation with sodium sulfide; and the hexagonal appears from weaker alkaline solution, hence by precipitation with ammonium sulfide. From manganese acetate solution and ammonium sulfide one obtains chiefly the cubic or chiefly the hexagonal rose sulfide, depending on the acetate concentration; the hexagonal crystals predominate from dilute solutions and the cubic from almost saturated solutions. The lattice constant of the β-hexagonal form is 3.976; of the β-cubic form, 5.600.

A red or orange manganese sulfide is said to precipitate from a weakly acid solution of a manganese salt by the prolonged action of hydrogen sulfide.[11] Olsen and Rapelje [12] claim that the ordinary flesh-colored sulfide is a mixture of the red sulfide with a gray form. Actually, x-ray analysis shows the gray sulfide to be a mixture of green α-sulfide and the red β-modification.

Manganese, cadmium, and zinc sulfides all may assume both the zinc blende and wurtzite structure. The two modifications of cadmium sulfide form a complete series of mixed crystals with the respective modifications of β-manganese sulfide. On the other hand, with the sulfides of zinc and manganese a miscibility gap extending from about 20–84 atomic per cent manganese is indicated.[13] Precipitates in this

[9] Tower and Chapman: J. Phys. Chem., **35**, 1474 (1931); Tower: **40**, 599 (1936).

[10] *Cf.* Schnaase: Z. physik. Chem., **B20**, 89 (1933); Naturwissenschaften, **20**, 640 (1932).

[11] Volker: Ann., **59**, 27 (1846); Fisher: J. Russ. Phys.-Chem Soc, **46**, 1481 (1914).

[12] J. Am. Chem. Soc, **26**, 1615 (1904).

[13] Schnaase: Z. physik. Chem., **B20**, 89 (1933).

gap consist of two separate phases having compositions corresponding to the above limits. The mixed crystals are chiefly of the zinc blende type, but some having a wurtzite structure were also observed.

The evidence from adsorption studies and from x-ray analysis of the precipitates argues against the view of Landesen that the rose sulfide which turns green spontaneously is an ammonium sulfo salt of the composition $NH_4HMn_3S_4$ or any definite compound other than manganous sulfide. Landesen [14] attributes the failure to find his alleged complex compounds by x-ray analysis methods to the fact that they are instable except in contact with the mother liquor and are therefore decomposed by the washing and drying operations incident to preparing the samples for analysis. This question could be settled definitely by x-ray analysis of the fresh moist gels obtained under varying conditions.

A disulfide of manganese having the pyrite structure may be precipitated from aqueous solutions at high temperatures (around 160°).[15] In the x-ray diagrams from certain mixtures of manganese and cadmium sulfides, Schnaase observed lines corresponding to the higher sulfide of manganese and suggested that excess sulfur not removable by carbon disulfide from certain manganous sulfide precipitates may be present as manganese disulfide.

COLLOIDAL NICKEL SULFIDE

The Precipitated Salt

It is a well-known fact that nickel and cobalt sulfides are not precipitated by hydrogen sulfide in dilute hydrochloric acid solution, and yet the precipitates from alkaline solution are insoluble in dilute acid after standing for a time. Thiel and coworkers [16, 17] found that different methods of preparation and treatment of nickel sulfide gave products that varied greatly in their solubility in hydrochloric acid. They were thus led to assume the existence of three so-called modifications designated as α-, β-, and γ-forms having more or less definite solubilities in hydrochloric acid of a given strength. From Thiel's point of view the α-form of a given preparation is all the sulfide which is quickly and easily soluble in cold 2 *N* HCl; the β-sulfide is the part soluble in hot 2 *N* HCl; and the γ-sulfide is the remainder. It is prob-

[14] Z. anorg Chem, **216**, 114 (1933).
[15] Senarmont: Ann. chim phys., (3) **30**, 140 (1850).
[16] Thiel and Ohl: Z. anorg. Chem, **61**, 396 (1909).
[17] Thiel and Gessner: **86**, 1 (1914); *cf.* Herz: **27**, 390 (1901).

able that these three alleged isomeric forms of nickel sulfide are merely stages in the continuous transformation from the soluble to the insoluble state. There is no inversion point between any two of the alleged isomers, and it is quite likely that any number of substances with intermediate properties could be formed. As frequently observed with the hydrous oxides, the very finely divided soluble and readily peptized particles of the newly formed precipitate go over gradually and continuously into larger and denser particles which are less soluble and less readily peptized. This change in physical character is always more rapid in contact with a medium which possesses a slight solvent action.

Cone, Renfrew, and Edelblute [18, 19] found the initial rate of solution in a given concentration of hydrochloric acid to depend on the concentration of hydrogen sulfide in the system. This is probably connected with the adsorption of hydrogen sulfide, which is greater for nickel sulfide than for cadmium, lead, and iron sulfides, and increases with the hydrogen sulfide concentration. Because of this adsorption, nickel sulfide precipitates contain more or less excess sulfide. The optimum *p*H value for the analytical precipitation of nickel as sulfide is 4.4, which may be maintained by an ammonium acetate-acetic acid buffer.[20]

Nickel Sulfide Sols

Unlike the sulfides of iron and cobalt, nickel has a marked tendency to form colloidal solutions, especially in the presence of an excess of ammonium sulfide. Every analyst is familiar with the dark brown coloration which forms gradually in a nickel salt solution to which ammonium sulfide is added. Many investigators have attributed this coloration to the formation of a sulfo salt [21] resulting from the presence of an excess of sulfur in the ammonium sulfide reagent. This view was proved to be erroneous by Thiel and Ohl,[16] who obtained the familiar brown-colored solution using ammonium sulfide entirely free from polysulfide. They attributed the gradual development of the brown color to polymerization of nickel sulfide with the ultimate formation of a sol. As already indicated, it is likely that the phenomenon results from gradual growth of the sulfide particles rather than from

[18] J. Am Chem. Soc, **57**, 1434 (1935).

[19] *Cf.* Middleton and Ward: J. Chem. Soc, 1459 (1935).

[20] Haring and Westfall: J. Am. Chem. Soc, **52**, 5141 (1930).

[21] Lecrenier: Chem.-Ztg., **13**, 431, 449 (1889); de Koninck and Ledent: Z. angew. Chem., **5**, 203 (1891); de Koninck: Compt. rend., **120**, 735 (1895); Villiers: **119**, 1208, 1263 (1894); Antony and Magri: Gazz. chim. ital., **31** II, 265 (1901).

the formation of polymers. There is no doubt, however, that the color results from nickel sulfide in colloidal solution. Thorne and Pates [22] proved this conclusively when they ultrafiltered out the brown color completely from a sol prepared with the ordinary laboratory reagents.

An investigation of the factors influencing the formation of the brown sol was made by passing hydrogen sulfide directly into a nickel ammonium hydroxide solution, thereby avoiding the presence of any polysulfide. When the ammonia concentration is 100 g/l, a sol is formed with a nickel concentration between 2.0 and 0.01 g/l. Some precipitate results on standing if the nickel concentration exceeds 1.0 g/l; below 0.1 g/l no coloration is observed. The range of nickel concentration between which a sol is formed is determined by the ammonia concentration. For a sol containing 0.3 g of the metal per liter, the ammonia concentration may be reduced to 45 g/l; for 0.2 g nickel, 10 g ammonia per liter; and for 0.1 g nickel, 5 g ammonia per liter. In every case, the sol must be kept saturated with hydrogen sulfide to prevent any precipitation; if the hydrogen sulfide is removed completely, precipitation results, but the precipitate is repeptized in part by adding more hydrogen sulfide even if the sulfide is allowed to age for several months. Moreover, the black residue obtained by taking the sol to dryness in a vacuum desiccator is partly repeptized by suspending in water and treating with ammonia and hydrogen sulfide.

The sol is quite stable in the absence of air. Boiling to remove hydrogen sulfide causes precipitation, but the excess gas may be washed out with hydrogen or the excess ammonia removed in a vacuum desiccator without precipitation. The particles are negatively charged, but alkali salts exert no precipitating action even in high concentration. Salts with multivalent cations cannot be used since they react either with the ammonia or the hydrogen sulfide.

To prevent the formation of the nickel sulfide sol in qualitative analysis, Pan and Tang [23] recommend neutralizing the test solution with nitric acid and making just alkaline with ammonia before conducting in the hydrogen sulfide.

Stable brown sols of nickel sulfide are not obtained in the presence of an excess of ammonium polysulfide; instead, a black precipitate is formed which cannot be washed without decomposition.[24] Analysis of an unwashed sample indicates a composition between NH_4NiS_4 and NH_4NiS_5; but the constitution is indefinite. It may be a sulfo salt

[22] Kolloid-Z., **38**, 155 (1926).
[23] Nanking J., **4**, 33 (1934).
[24] Ephraim: Ber., **56B**, 1885 (1923).

like the copper compound NH_4CuS_4,[25] the ordinary nickel sulfide with adsorbed polysulfide, or a higher sulfide of nickel.

Villiers[26] developed a test for nickel which depends upon the formation of the brown sol. The nickel salt solution is treated with tartaric acid and a slight excess of sodium hydroxide. On passing in hydrogen sulfide, a part of the nickel sulfide is peptized, giving the characteristic dark brown color. Cobalt ions are precipitated as cobalt sulfide by this treatment except when a trace is present and this sulfide is likewise peptized, giving a brown sol.[27] Tower showed that tartrate is essential for the stability of nickel sulfide sols prepared in alkali tartrate solution, complete precipitation resulting on removal of the organic ion by dialysis. A sol formed in the presence of glycerin[28] is likewise thrown down by dialyzing out the organic stabilizing agent.

COLLOIDAL COBALT SULFIDE

The gel and sol of cobalt sulfide are obtained by the same procedures used for nickel sulfide. As already noted, the tendency of the gel to be peptized by ammonium sulfide is slight, but a dilute sol results by passing hydrogen sulfide into a cobalt solution containing an alkali tartrate.

From colorimetric analysis of nickel and cobalt (M) sulfide sols using a selenium cell, Mickwitz[29] concludes that the sols formed from dilute solutions with sodium sulfide have the composition $M(OH)(SH)$; with excess hydrogen sulfide, the solid phase in the cobalt sulfide sol is believed to be $Co(SH)_2$.[19] The evidence for these conclusions is altogether inadequate. It is probable that, if the sols were examined directly by x-ray diffraction methods as described by Weiser and Milligan,[30] they would give the pattern of MnS and CoS, respectively.

The quantitative precipitation of cobalt as sulfide is accomplished at a pH of 3.9 maintained by an ammonium acete-acetic acid buffer.[31] Riegel[32] describes the phenomena connected with the precipitation of cobalt sulfide bands in silica gel.

[25] Gluud: Ber, **55B**, 952 (1922); Gluud and Mühlendyck: **56B**, 899 (1923).

[26] Compt. rend., **119**, 1263 (1894); **120**, 46 (1895).

[27] Tower: J. Am. Chem. Soc., **22**, 501 (1900); Tower and Cooke: J. Phys Chem., **26**, 728 (1922); *cf.* Dumanskii and Buntin: J. Russ. Phys.-Chem. Soc., **61**, 279 (1929).

[28] Müller and Artman: Oesterr. Chem.-Ztg., **7**, 149 (1904).

[29] Z. anorg. Chem., **196**, 113 (1931).

[30] J. Phys. Chem., **40**, 1095 (1936).

[31] Haring and Leatherman: J. Am. Chem. Soc., **52**, 5135 (1930).

[32] J. Phys. Chem., **35**, 1674 (1931).

COLLOIDAL IRON SULFIDES

The black precipitate of ferrous sulfide thrown down from a cold ferrous salt solution with ammonium sulfide is quite finely divided and may be peptized in part by thorough washing with cold water. The sol is rather instable, as is the one formed by passing hydrogen sulfide into a very dilute solution of a ferrous salt.[33] The stability is very much increased if the reaction is carried out in the presence of glycerin,[28] gelatin, or sugar. Sabbatani [34] investigated the pharmacological action of such sols when administered to dogs and rabbits. Since the particles were protected by an adsorbed film, the preparations were inactive so long as they remained colloidal.

Ferric sulfide is apparently formed [35] both by the action of ammonium sulfide on a ferric salt and of ammonium polysulfide on a ferrous salt. The precipitate behaves toward ammoniacal zinc solution as if it were Fe_2S_3; but toward mercuric chloride it reacts as follows: $FeS\ FeS_2 + 2HgCl_2 \rightarrow 2HgS + S + 2FeCl_2$. It is suggested that ferric sulfide may exist either as Fe_2S_3 or as $FeS \cdot FeS_2$; this is termed valence isomerism. With freshly precipitated hydrous ferric oxide and ammonium sulfide, Fe_2S_3 results chiefly; whereas, with ferric tartrate and ammonium sulfide, a double salt, $Fe_2S_3(NH_4)_2S$, is said to form.[36] The accuracy of these statements should be checked by x-ray analysis of the products.

A sol of ferric sulfide is said to form by passing hydrogen sulfide into a dilute solution of hydrous ferric oxide in tartaric acid. On adding to a sodium sulfide solution either ferric chloride or ferrous sulfate followed by oxidation with sodium or hydrogen peroxide a dark green sol is obtained which gives a dark green gel on coagulating with sodium chloride.[37] Although the ratio of iron to sulfur in the gel may be represented by Fe_2S_3, it is believed that the sol consists of dispersed thioferrites. The color of the sulfur waters in Yellowstone National Park is attributed to the dispersed iron compound, whatever it may be.

[33] Winssinger: Bull. soc. chim., (2) **49**, 452 (1888).

[34] Atti accad Lincei, (5) **32** II, 326, 473 (1923); **33** I, 8; II, 228 (1924).

[35] Feigl: Z. anal. Chem., **72**, 32 (1927).

[36] Feigl and Backer: Z. anal. Chem., **74**, 393 (1928); *cf., however,* Pearson and Robinson: J. Chem. Soc., 814 (1928).

[37] Casares: Anales soc. españ. fís. quím., **31**, 638 (1933).

COLLOIDAL INDIUM TRISULFIDE

Yellow indium trisulfide is precipitated by conducting hydrogen sulfide into a solution of an indium salt which is neither too acid nor too concentrated.[38] If indium hydroxide is suspended in water through which hydrogen sulfide is passed, a golden-yellow negative sol of the sulfide is produced.[39] This sol may be boiled to remove excess hydrogen sulfide without flocculation, but it is quite instable in the presence of electrolytes, especially those with strongly adsorbed cations.

COLLOIDAL THALLOUS SULFIDE

Thallous sulfide, Tl_2S, is precipitated in a finely divided hydrous condition when hydrogen sulfide or ammonium sulfide is added to an alkaline or acetic acid solution of a thallous salt. Incomplete precipitation of the hydrous sulfide results when hyposulfite is added to a thallous salt solution; formed in this way the mass is reddish brown at first, then violet, and finally black.[40] If the cold solution from which the salt separates contains a trace of free sulfuric acid, it comes down as microscopic tetrahedra.[41] The sol of thallous sulfide is prepared by passing hydrogen sulfide into a very dilute solution of a thallous salt and dialyzing the product.[33]

Thallic sulfide, Tl_2S_3, is not precipitated by the action of hydrogen sulfide on an aqueous solution of a thallic salt, for, if formed at all, it is reduced instantly to thallous sulfide and free sulfur.[42]

COLLOIDAL SULFIDES OF GERMANIUM

Germanous sulfide, GeS, is precipitated as a hydrous mass when hydrogen sulfide is passed into a solution of germanous chloride.[43] If the precipitation is carried out in the hot, the sulfide is dark red in color and granular; if precipitated in the cold, it is light yellow and gelatinous. The granular product is definitely crystalline, but the gelatinous product is said to be amorphous.[44] It is probable, however, that x-ray

[38] Winkler: J prakt Chem, **94**, 1 (1865); **102**, 273 (1867); *cf* Thiel and Luckmann Z. anorg Chem, **172**, 353 (1928).

[39] Linder and Picton: J Chem Soc, **61**, 134 (1892).

[40] Brunck: Ann, **336**, 281 (1904).

[41] Hebberling: Ann., **134**, 11 (1865).

[42] Strecker: Ann., **135**, 207 (1865).

[43] Winkler. J. prakt. Chem., (2) **34**, 177 (1886); **36**, 177 (1887).

[44] Dennis and Hulse: J. Am. Chem Soc., **52**, 3553 (1930); *cf., also,* Dennis and Joseph: J. Phys. Chem, **31**, 1716 (1927); Pugh: J. Chem. Soc., 2369 (1930).

analysis would show the gel particles to have an orthorhombic crystalline structure [45] identical with the darker granular preparation. If the crystalline monosulfide is dissolved in potassium hydroxide and this solution neutralized with hydrochloric acid, the monosulfide comes down in a finely divided state [46] which hydrolyzes readily in water or moist air. The freshly formed precipitate of germanous sulfide is readily peptized by washing, giving an orange-red to brown sol which is quite stable if kept out of contact with air. The sol is negatively charged and is readily flocculated by acids and by salts with multivalent cations.

A study of the absorption band spectrum of germanous sulfide disclosed the germanium isotopes of atomic weight 76, 74, 72, and 70.[47]

Germanic sulfide, GeS_2, is thrown down by hydrogen sulfide from strongly acid solutions of germanium dioxide. An aqueous solution of the dioxide gives no precipitate with hydrogen sulfide, and the precipitation is incomplete from a slightly acidified solution; Johnson and Dennis [48] found the precipitation to be very nearly complete in 24–48 hours. The sulfide comes down at first in a very finely divided form giving the suspension a milky, almost colloidal, appearance; but, on standing, the white precipitate agglomerates to a flocculent form that is peptized by thorough washing to give an opalescent negative sol. The salt is hydrolyzed to some extent even in the cold; hence, when the sol is flocculated by heavy-metal salts, the coagulum has the color of the heavy-metal sulfides. In boiling water, complete hydrolysis takes place, giving a solution of GeO_2. Advantage may be taken of this property in the analytical determination of germanium.[49]

COLLOIDAL MOLYBDENUM SULFIDES

The trisulfide of molybdenum, MoS_3, is precipitated when hydrogen sulfide is passed into a concentrated solution of a molybdate followed by the addition of hydrochloric acid. It is also formed by boiling the molybdate of an alkali metal for a short time with ammonium sulfide and then precipitating with dilute mineral acid. Winssinger [33] prepared the sol by adding to a dilute solution of potassium sulfo-

[45] Zachariasen: Phys. Rev., **40**, 917 (1932).

[46] Johnson and Wheatley: Z. anorg. Chem., **216**, 273 (1934).

[47] Shapiro, Gibbs, and Laubengayer. Phys. Rev., **40**, 354 (1932).

[48] J. Am. Chem. Soc., **47**, 790 (1925); Dennis and Papish: **43**, 2131 (1921); *cf.* Johnson and Wheatley: Z. anorg. Chem., **216**, 273 (1934); Winkler: J. prakt. Chem., (2) **34**, 228 (1886).

[49] Müller and Eisner: Ind. Eng. Chem., Anal. Ed., **4**, 134 (1932).

molybdate slightly more than enough acid to liberate the sulfide and dialyzing. The transparent brown sol was quite stable; but if the preparation was not purified by dialysis it coagulated in a few hours.

Hydrous molybdenum pentasulfide is precipitated as a brownish-black mass by reducing with zinc an ammonium molybdate solution containing 20% H_2SO_4 and passing in hydrogen sulfide.[50] No sol of this sulfide has been described.

Svedberg [51] prepared a sol of molybdenum disulfide in isobutyl alcohol by passing an oscillating discharge between electrodes of molybdenite; in a similar way, von Hahn [52] prepared a blue hydrosol. A sol was also formed by cathodic disintegration of the molybdenum mineral.[53]

COLLOIDAL TUNGSTEN TRISULFIDE

The trisulfide of tungsten, WS_3, is precipitated by adding acid to a solution of tungsten trioxide in ammonium sulfide or by saturating an aqueous solution of a tungstate with hydrogen sulfide and acidifying. The precipitate is much more finely divided than the corresponding molybdenum salt and runs through the filter during washing. If the washed sulfide is suspended in boiling water, it is largely peptized, forming a brown sol. Winssinger prepared the sol by adding slightly more acid to a sodium thiotungstate solution than is necessary to free the sulfide. The color of the sol changes from a bright orange-red to a dark brown without agglomerating.

COLLOIDAL SELENIUM SULFIDE

Several substances have been described as compounds of selenium and sulfur, but they have all proved to be mixtures of the two elements,[54] which are known to form several series of mixed crystals.[55] It is possible, however, that the sol formed by conducting hydrogen sulfide into an aqueous solution of selenium dioxide [56] may contain

[50] Kruss: Ann., **225**, 1 (1884); Mawrow and Nikolow: Z. anorg. Chem, **95**, 188 (1916).

[51] "Die Methoden zur Herstellung kolloider Lösungen," 2nd ed., 490 (1909).

[52] Kolloid-Z. (Zsigmondy Festschrift), **36**, 277 (1925)

[53] Muller and Lucas: Z. Elektrochem., **11**, 521; Le Blanc: 813 (1905).

[54] Divers and Schimidzu: Chem. News, **51**, 199 (1885).

[55] Ringer: Z. anorg Chem., **32**, 183 (1902); Retgers: Z. physik. Chem., **12**, 583 (1893).

[56] Gutbier: Z. anorg. Chem., **32**, 292 (1902); Gutbier and Lohmann: **42**, 325 (1904); **43**, 384 (1905).

some selenium sulfide. In any event, the preparation is always referred to as colloidal selenium sulfide. The sol possesses a bright yellow color in reflected light and red in transmitted light. It is very stable even in the presence of electrolytes, but by adding hydrochloric acid and boiling, or by exposure to light, a plastic red gel is precipitated.[57] Since selenium sol is red, it is possible that the red color of the coagulum is due to colloidal selenium dispersed in plastic sulfur. It should be possible to settle this point by x-ray analysis or by an ultramicroscopic examination of the gel.

COLLOIDAL TELLURIUM SULFIDES

Both tellurium disulfide, TeS_2, and tellurium trisulfide, TeS_3, are said to exist in the sol state when prepared and kept at low temperatures.[58] The disulfide sol is obtained by passing hydrogen sulfide into a cold solution of a tetravalent tellurium salt. During the gradual formation, the sol changes in color from yellow, orange, and reddish brown to black with a bluish opalescence. If the reagents are pure the sol is quite stable; it is precipitated by freezing as reddish-brown flocs which are repeptized after thawing.

The sol of so-called tellurium trisulfide is formed by passing hydrogen sulfide into a cold dilute solution of telluric acid. The dialyzed preparation appears perfectly clear in transmitted light with a light blue to gray-violet color; but in reflected light, it is cloudy and gray in color. Like the disulfide sol, it is quite stable and possesses similar properties. The similarity in behavior of the two sols would seem to indicate that both are primarily mixtures of colloidal tellurium and colloidal sulfur.

[57] Von Hahn: Kolloid-Z., **27**, 172 (1920).
[58] Gutbier: Z. anorg. Chem., **32**, 292 (1902).

CHAPTER XV

LITHOPONE AND OTHER SULFIDE PIGMENTS

General Characteristics of Pigments

Ordinary paints consist of three essential parts: the pigment, the medium or vehicle, and the drier or siccative. Pigments are finely divided insoluble powders; when mixed with suitable media they form paints. For oil paints, the media are usually vegetable drying oils, of which linseed oil is by far the most important and most commonly used. For water-color paints, the vehicle consists of such substances as honey, glycerin, dextrin, and aqueous sols of the gums. The driers are oxygen carriers which catalyze the oxidation of the oil; among the most important driers are suitable compounds of metals such as lead, manganese, and cobalt which have more than one valence. Certain pigments, notably litharge and white lead, possess the necessary siccative properties and a special drier is not required. In the pyroxylin lacquers, which dry by evaporation of a volatile solvent, the nitrocellulose is dispersed in such media as amyl acetate, *n*-butyl alcohol, and glycol esters.

An ideal pigment should be quite stable chemically and should not react with any material with which it is likely to come in contact, either in the vehicle or on the surface which it covers. Actually, few pigments fulfill these ideal requirements, for few substances are capable of standing the action of light and the atmosphere, pure and impure, for indefinite periods of time. Although it is obvious that no pigment is absolutely proof against destruction, it is equally true that all pigments are quite durable under certain conditions. The chemical characteristics which a pigment must possess are determined, therefore, by the conditions to which it will be subjected. In general, the most valuable pigments are to be found among the metallic oxides and the metallic salts of fairly strong acids.

In addition to the chemical requirements, a pigment must possess the desired color, covering power, hiding power, and oil-adsorption value.[1] Since the physical state of the pigment, including the particle

[1] *Cf.* Bartell and Hershberger: Ind. Eng. Chem., **22**, 1304 (1930).

size, has such a profound effect on the above characteristics, one must approach this subject from the standpoint of colloid chemistry. Many of the general principles involved are well illustrated by the colloidal sulfides.

ZINC SULFIDE AND LITHOPONE

Preparation and General Properties

Lithopone. Lithopone is a white pigment consisting of an intimate mixture of barium sulfate and zinc sulfide prepared in a special way. X-ray analysis of the material showed it to be a non-homogeneous mixture and not a solid solution or a compound.[2] The first patent was taken out for its preparation by De Douhit in France in 1850,[3] and it was given the name lithopone by Boulez in 1877. The process patented by Orr in 1874 consists in the double decomposition of barium sulfide and zinc sulfate in solution, followed by igniting the sulfide-sulfate precipitate and quenching in water. Before ignition, the precipitate is useless as a pigment, having very little covering power or body. Heating changes its physical character: first, by dehydrating the zinc sulfide; second, by rendering it brittle so that fine grinding is possible; and third, by increasing the density and thereby increasing the body of the pigment.

Since a suitable pigment cannot be prepared by grinding barium sulfate and zinc sulfide together, Mann [4] concludes that lithopone is not a mere mixture. A preparation having the properties of lithopone is formed by mixing a positively charged sol of barium sulfate with a negatively charged sol of zinc sulfide. Mann regards the mechanism of lithopone formation to be a mutual precipitation of oppositely charged colloids. Although mutual precipitation of colloidal barium sulfate and colloidal zinc sulfide gives a mixture with the desired physical character, it seems unnecessary to postulate the initial formation of oppositely charged colloidal particles to account for the nature of the product resulting from direct metathesis. The simultaneous condensation of barium sulfate and zinc sulfide molecules from solution will of itself give a more intimate mixture than could result from mutual precipitation of the sols, and it is probable that the former process gives the better product. One can obtain a more intimate mixture of barium and strontium carbonates by simultaneous precipitation than could result from grinding the two powders together. Like lithopone,

[2] Wood: J. Soc. Chem. Ind., **49**, 300*T* (1930).
[3] Cooper: Chemistry & Industry, **46**, 552 (1927).
[4] Colloid Symposium Monograph, **3**, 247 (1925).

the product resulting from simultaneous precipitation will differ in physical character from the mechanically mixed product; but the qualities of the simultaneously precipitated carbonates would not be attributed to mutual precipitation of oppositely charged particles. Moreover, the difficulty of preparing a positively charged hydrosol of barium sulfate precludes the possibility of its formation in the presence of an excess of either sulfate or sulfide ion.[5]

The ignition of lithopone in the air results in partial oxidation of the zinc sulfide to zinc oxide. Since the presence of much zinc oxide decreases the covering power of the pigment, the conditions of ignition are adjusted so as to prevent undue oxidation and the product is quenched in water.[6] Heating in the absence of oxygen has been suggested;[7] but, as will be pointed out later, the formation of a small amount of oxide on the surface of the zinc sulfide particles is an advantage in increasing the stability of the pigment to light. If the pigment contains too much oxide and is heated too high, it goes off-color, becoming yellowish instead of the desired pure white.[8] A "voluminous" lithopone has been prepared having an apparent volume 20% greater than ordinary types; it has higher oil-adsorption power, and paints containing it carry less pigment and have a lower hiding power.[9] Its lack of normal properties is the result chiefly of insufficient calcination.[10]

Theoretically, equivalent solutions of barium sulfide and zinc sulfate produce 29.5% ZnS and 70.5% $BaSO_4$. The composition of the commercial products is sometimes modified either by the addition of barytes or of zinc sulfide prior to the ignition. The tinctorial strength and hiding power of the pigment are reduced by adding barytes and are increased by adding zinc sulfide.

When properly prepared,[11] lithopone is one of the most important white pigments for paints and enamels and for compounding with rubber and linoleum. It is pure white, very fine in texture, and has the same tinctorial strength as zinc oxide and greater hiding power.[12]

[5] Weiser: J. Phys. Chem., **21**, 314 (1917).

[6] O'Brien: J. Phys. Chem., **19**, 113 (1915).

[7] Griffith: Brit. Pat. 3,864 (1877); Ostwald and Brauer: Ger. Pat. 202,709 (1908).

[8] *Cf.* Meyer: Ger. Pat. 246,021 (1908); Brase: 254,291 (1909); Englemann: 264,904 (1912); Eibner: 324,646 (1918); Steinau: Chem.-Ztg., **44**, 974 (1920); **45**, 741, 1238 (1921).

[9] Hebberling: Farben-Ztg., **38**, 619 (1933); Lins: Farbe u. Lack, 101 (1933).

[10] Seidel: Farbe u. Lack, 127 (1933).

[11] *Cf., for example,* Flynn, Stutz, and Schertzinger: U. S. Pat. 2,007,527 (1935); Flynn: 1,882,072; Hooey: 1,896,312; Stutz and Depew: 1,914,563 (1933).

[12] Toch: "Chemistry and Technology of Mixed Paints," 26 (1925).

Unlike white lead, it is non-poisonous, is unaffected by sulfurous gases, and is stable in every medium for paints except those of high acidity.[13] It mixes easily with oils and other colors. It is insoluble in water, ammonia, and alcohol, and is practically fireproof.[14]

Zinc Sulfide. Zinc sulfide alone is sometimes employed as a pigment under the name metal white or zinc white, although the latter term is more often applied to the oxide of zinc. When properly prepared, the sulfide possesses good hiding power and higher durability than lithopone [15] and, like zinc oxide, is not darkened by the action of sulfur or sulfur vapors. A large number of patents have been taken out for the technical production of the pigment; thus, a fine white product is obtained by the action of sodium sulfide on an alkaline solution of sodium zincate.[16] A powder which does not mat together on drying results if the precipitation is carried out at 195° under pressure.[17] Good products are reported from the action of sulfur [18] or of carbon disulfide [19] on an alkaline solution of zinc oxide. It is also obtained from zinc blende or other zinc-bearing ores;[20] indeed, zinc blende has been finely pulverized and used directly without further treatment.[21] It is also formed in the dry way by bringing together the vapors of the two elements and by calcining zinc sulfate under suitable conditions.[22] Work and Odell [23] showed that the development of pigment value measured by covering power and tinting strength is associated with growth of particles to visible range of sizes by suitable ignition; the maximum pigment value results by heating at 600°.

A satisfactory pigment must be stable in the light and must possess a pure white color. When formed by precipitation methods, the adsorbed water can be removed only at relatively high temperatures. On ignition in the air, the pigment assumes a yellow color which has been attributed to the formation of an oxysulfide [24] but which is probably

[13] Morrell and Waele: "Rubber, Resins, Paints, and Varnishes," 118

[14] Scott: "White Paints and Painting Materials," 237.

[15] Nelson: Am. Paint J., **15**, No. 28, 20*f* (1931).

[16] De Stucklé: Ger. Pat. 171,872 (1906).

[17] Goldschmidt and Sohn: Ger. Pat 262,701 (1912).

[18] Pipereaut and Vila: Ger. Pat. 223,837 (1907).

[19] Desachy: Brit. Pat. 126,627 (1919).

[20] Thwaites: Ger. Pat. 222,291 (1908); Brit. Pat. 9,175 (1912); J. Soc. Chem. Ind, **31**, 431 (1912); Clerc and Nihoul: Ger. Pat. 381,423 (1920).

[21] Richter· Farben-Ztg., **29**, 728 (1924).

[22] Pipereaut and Helbronner: U. S. Pat. 1,443,077 (1922); Helbronner: Brit. Pat. 148,351 (1920); Comment: U. S. Pat. 1,374,435 (1921).

[23] Ind. Eng. Chem., **25**, 411, 543 (1933).

[24] De Stucklé: J. Soc. Chem. Ind., **30**, 96 (1911).

zinc oxide, since the latter is known to be yellow when sintered.[25] The color may be removed[24] by heating with NH_4HS at 155°, by treating with hydrogen sulfide in the presence of hydrofluoric acid, or by heating with 2% H_2SO_4.[26]

Darkening of Zinc Sulfide Pigments in Light

Unless special precautions are taken in the manufacture of zinc sulfide pigments, they blacken in the sunlight and become white again in the dark. Attention was first called to this phenomenon by Phipson,[27] who observed that a gatepost painted white with lithopone turned dark during the day and became white again at night. The barium sulfate in lithopone is without influence or plays but a minor rôle in the process since zinc sulfide alone will exhibit the same phenomenon. Because of the importance of this behavior from both a theoretical and technical standpoint, the cause of the blackening and the mechanism of the process will be considered in some detail.

Cause of the Darkening

Phipson, who first investigated the darkening of lithopone, claimed that it was not caused by the presence of impurities which form black sulfides, and so was led to attribute the discoloration to the presence of a new element, similar to lanthanum, which he named actinium. This hypothesis was disproved by Cawley,[28] who concluded, by a process of elimination, that the black color resulted from a small amount of finely divided zinc. The first experimental evidence to support this assumption was obtained in Bancroft's laboratory by O'Brien,[6] who brought some of the blackened lithopone in contact with a ferric alum-potassium ferricyanide solution and obtained a blue coloration such as would be expected in the presence of metallic zinc. Later, Durst[29] showed that a blackened lithopone became permanently black if brought in contact with a solution of nobler metals such as copper and lead, probably owing to the displacement of the heavy metal from solution by metallic zinc. It should be pointed out, however, that this evidence is not altogether conclusive since salts of noble metals may react with zinc sulfide directly. Thus, silver chloride reacts quantitatively with precipitated zinc sulfide in accordance with the

[25] Farnau: J. Phys. Chem., **17**, 639 (1913).
[26] Koetschet and Meyer: U. S. Pat. 1,001,415 (1911).
[27] Chem. News, **43**, 283; **44**, 73 (1881).
[28] Chem. News, **44**, 51, 167; *cf.* Orr: 12 (1881).
[29] Z. angew. Chem., **35**, 709 (1922).

reaction: $ZnS + 2AgCl \rightarrow ZnCl_2 + Ag_2S$ (black).[30] All doubt as to the cause of blackening was removed by Job and Emschwiller,[31] who obtained several centigrams of zinc by the action of the light from a quartz mercury lamp on a light-sensitive zinc sulfide suspended in water in a quartz vessel. The metal evolved hydrogen from acids and displaced copper from copper sulfate. Simultaneously with the liberation of zinc, sulfur was formed which was extracted with carbon disulfide and subsequently crystallized from the solution. Besides the primary products, zinc and sulfur, a small amount of zinc thionate and hydrogen were formed, the latter probably resulting from the slight decomposition of water by the colloidal zinc.

In opposition to the view that the darkening is due to colloidal zinc, Eibner[32] claims that the discoloration is caused by the presence of metals which form black sulfides. This view is altogether untenable: first, because chemically pure zinc sulfide is blackened by light;[33] and second, because the addition to lithopone of a metallic salt such as lead acetate has no appreciable influence on the tendency to darken in light.[34]

Conditions for Photochemical Decomposition

Crystal Structure. Zinc sulfide precipitated from ammoniacal solution with hydrogen sulfide or ammonium sulfide consists of minute cubic crystals corresponding to zinc blende or sphalerite. Under ordinary conditions the precipitated sulfide is stable but is rendered light-sensitive by ignition under such conditions that wurtzite is formed. A second requirement for light sensitivity is the presence of an excess of water. Specially prepared, chemically pure zinc sulfide[35] will darken, so that impurities are not essential to the process, although certain salts, especially soluble zinc salts, increase the light sensitivity. Indeed, an unignited zinc blende formed slowly from slightly acid solution will darken on exposure to light in contact with a zinc chloride solution.[36]

The much greater light sensitivity of wurtzite was recognized almost 50 years ago by Cawley,[37] who pointed out that zinc blende will

[30] Jander and Stuhlmann: Z. anal. Chem., **60**, 308 (1921).
[31] Compt rend, **177**, 313 (1923).
[32] Farben-Ztg., **27**, 3378 (1922); Chem.-Ztg, **47**, 13 (1923)
[33] Lenard: Ann. Physik, (4) **68**, 553 (1922).
[34] Maass and Kempf: Z. angew. Chem, **36**, 294 (1923).
[35] Tomaschek: Ann Physik, (4) **65**, 189 (1921).
[36] Weiser and Garrison: J. Phys. Chem., **31**, 1237 (1927).
[37] Chem. News, **63**, 88 (1891).

not darken in ultraviolet light. This conclusion was confirmed by Schleede [38] from observations with pure precipitated zinc sulfide thrown down from alkaline solution. When ignited below 850° the sulfide was not darkened by long exposure to quartz ultraviolet light, and an x-radiogram showed it to consist of the cubic crystals of sphalerite. Ignition at 1150° (35° below the melting point of wurtzite) gave a product with the maximum light sensitivity, and an x-radiogram showed it to be hexagonal wurtzite. Ignition at 1000° gave a mixture of both blende and wurtzite which darkened less readily than pure wurtzite (see second paragraph below). The presence of copper, manganese, or cadmium in amounts necessary to cause phosphorescence had no effect on the light sensitivity.

By carrying out the ignition in the presence of a flux, Schleede found the ignition temperature to be of secondary importance. Thus, when the sulfide was ignited at as low a temperature as 750° in the presence of potassium chloride, an x-radiogram showed the formation of some wurtzite and even glass ultraviolet light caused darkening. Since Schleede did not know the mechanism of the darkening process, he attributed the light sensitivity in the presence of chloride to the formation of mixed crystals of wurtzite and the halogen. Washing out the chloride destroyed the sensitivity to glass ultraviolet light but did not affect the action toward quartz ultraviolet light. Ignition with both chlorides and bromides gave light-sensitive products, but ignition with fluorides, phosphates, and borates gave light-stable preparations. This is in line with O'Brien's [6] findings, that the addition of phosphates, ferrocyanides, borates, cyanides, or bicarbonates to lithopone prevented the darkening or decreased it to an appreciable extent.

Although wurtzite content and light sensitivity of zinc sulfide frequently go hand in hand, it was found at the New Jersey Zinc Company [39] that certain zinc sulfides with very high wurtzite content are very light-resistant. It was suggested, therefore, that it was not the wurtzite form or the sphalerite form which was light-sensitive but was the unstable zones at the boundaries between two dissimilar crystals.

Moisture. Cawley,[37, 40] who suggested that the darkening of zinc sulfide was caused by metallic zinc and who first pointed out that ordinary zinc blende is non-sensitive to light, likewise was the first to recognize the importance of the presence of moisture for the black-

[38] Z. physik. Chem., **106**, 391 (1923).
[39] Private communication from Dr. Howard M. Cyr.
[40] *Cf.* O'Brien: J. Phys. Chem., **19**, 126 (1915).

ening. Lenard [41] and Schleede [42] called attention to the fact that more than a trace of moisture is necessary. Indeed the blackening is more marked when the surrounding air is supersaturated with moisture than when it is saturated, and the effect is still more pronounced when the sulfide is covered with water. The reason for this will be discussed in a later section.

Relation to Phosphorescence. Since the action of light on phosphorescent zinc sulfide is usually accompanied by blackening [43] which disappears in the dark, some investigators conclude that the phenomena of luminescence and darkening are intimately related. Thus Job and Emschwiller [31, 44] give phosphorescence as one of the requirements for a light-sensitive sulfide. Lenard showed, however, that a chemically pure, non-phosphorescent sulfide will blacken in the light and that a fairly dry phosphor will glow without darkening, the latter phenomenon manifesting itself only in the presence of an excess of water vapor. Moreover, the blackening of a number of zinc phosphors was found to require a shorter wave length of light than was needed to excite phosphorescence. Thus the darkening appeared suddenly at a wave length of 334 mμ while intense phosphorescence maxima were observed by radiations of 430 and 360 mμ, which caused no darkening. It appears, therefore, that the two phenomena are not necessarily related although they are produced simultaneously by proper excitation. As is well known, the darkening of the silver halides by light is not accompanied by phosphorescence.

Mechanism of the Darkening Process

Since zinc sulfide which has not been ignited will not blacken ordinarily, Cawley suggested that the ignition results in the formation of some zinc oxide with which the remaining zinc sulfide reacts in the light, as follows: $ZnS + 2ZnO \rightarrow SO_2 + 3Zn$. This view is untenable, since ignition of lithopone under conditions favorable for forming a film of zinc oxide over the sulfide particles gives a light-stable product, whereas removal of the zinc oxide film from such a preparation by heating with an acid restores the light sensitivity.[6, 34] Furthermore, chemically pure zinc sulfide is darkened by light. Maass and Kempf [34] believed that the darkening is occasioned by the following reaction:

[41] Ann. Physik, (4) **68**, 572 (1922).

[42] Z. physik. Chem., **106**, 390 (1923).

[43] Lenard: Ann. Physik, (4) **31**, 652 (1910); Baerwald: **39**, 849 (1912); Tomaschek: **65**, 195 (1921).

[44] Loeb and Schmiedeskamp: Proc. Natl. Acad. Sci. U. S., **7**, 202 (1921).

$2ZnS \rightarrow ZnS_2 + Zn$. This is likewise untenable since sulfur instead of the hypothetical zinc disulfide is formed in the process.

Lenard explained the necessity for ignition by postulating the formation of polymerized molecules, $(ZnS)_x$, which were assumed to blacken owing to the "liberation or loosening of zinc atoms from the molecular union." The subsequent discoloration in the dark was attributed to the recombination of the loosened zinc and sulfur atoms. This mechanism is not satisfactory since it is based on some assumptions of doubtful accuracy and since it does not accord with all the experimental observations. In the first place, the formation of polymerized molecules of zinc sulfide has not been proved. Moreover, it is questionable whether a "loosened" atom of zinc would cause darkening, and it is known definitely that free atoms of zinc are formed. Finally, Lenard's assumption that the blackening-discoloration process is reversible is not in accord with the experimental facts to be recounted in the next section.

Effect of Soluble Zinc Salts. It has been known for a long time that a soluble silver salt, such as silver nitrate, increases the light sensitivity of silver bromide (p. 146), and Cawley and O'Brien observed a very marked increase in sensitivity of lithopone in the presence of soluble zinc salts.

The sensitizing action of silver nitrate on silver bromide has been accounted for in part by assuming that the soluble salt acts as a bromine acceptor reacting with the bromine in accord with the equation: $Br_2 + AgNO_3 + H_2O \rightarrow AgBr + BrOH + HNO_3$; but no such mechanism can be assumed for the sensitizing action of zinc chloride on zinc sulfide. In the light of Fajan's observation on the effect of adsorbed silver ions on the photosensitivity of silver halides (p. 148), it seems altogether probable that adsorbed zinc ions would increase the photosensitivity of zinc sulfide by increasing the number of elementary processes. This means that, if the surface were covered with adsorbed zinc ions, then an equal amount of zinc sulfide will absorb a larger portion of the incident light and therefore more zinc sulfide will be decomposed.

Since a salt always shows a strong tendency to adsorb its own ions, there is little doubt that zinc ions will be preferentially adsorbed at a zinc sulfide surface, just as silver ions are adsorbed at a silver halide surface. From this point of view, any factor which favors the formation of zinc ions in the immediate region of the surface of zinc sulfide will tend to increase its sensitivity toward light. As a matter of fact, soluble zinc salts have a pronounced sensitizing action, whereas in-

soluble zinc salts have little effect; moreover, ignition in the presence of a small amount of chloride or bromide which forms soluble zinc salts favors the blackening, whereas ignition with fluorides, phosphates, or borates which form insoluble salts retards or prevents blackening.[6]

The Rôle of Water. From the above consideration it follows that the rôle of water in the photochemical decomposition of zinc sulfide is merely that of an ionizing solvent for the sulfide and for adsorbed zinc salts, yielding zinc ions which are adsorbed on the surface of the sulfide lattice and sensitize it. As has been pointed out, natural zinc blende and precipitated blende are ordinarily light-stable whereas wurtzite is decomposed by ultraviolet light. The difference in behavior is readily understood when one recalls that wurtzite is 4.5 times as soluble as blende.[45] This means not only that the stability of the wurtzite lattice is the smaller but also that it yields more readily the zinc ions which may play such an important part in the darkening process.

Since a solution of a suitable acid or zinc salt increases the sensitivity of wurtzite enormously, it seemed likely that precipitated zinc sulfide might be made to darken under suitable conditions. This proved to be true.[46] A 20% solution of recrystallized zinc sulfate was treated with ammonia short of precipitation, and a stream of specially purified hydrogen sulfide[47] was passed into the solution very slowly until precipitation ceased. In this way, fairly large crystals were formed in the presence of an excess of zinc ion since the precipitation was incomplete, stopping when the hydrogen ion concentration became too high. The sulfide, after being freed from excess sulfate, was exposed to quartz ultraviolet light in contact with zinc chloride, and prompt blackening resulted. A sample of the gelatinous sulfide, precipitated rapidly with ammonium sulfide, did not blacken in the presence of zinc chloride. A distinct crystal structure is therefore essential to light sensitivity.

Since the preferential adsorption of zinc ions sensitizes the sulfide, it seemed possible that the presence of a salt such as sodium sulfide, the anion of which is more strongly adsorbed than the cation, would stabilize the sulfide. Actually, the sensitivity of zinc sulfide to light was decreased enormously in the presence of sodium sulfide. For example, a sensitive sulfide covered with water was blackened by a 2-minute exposure to quartz ultraviolet light whereas the same preparation covered by a sodium sulfide solution as dilute as 0.02 *N* showed no signs

[45] Gmelin: "Handbuch anorg. Chem.," 8th ed., **32**, 201 (1924).
[46] Weiser and Garrison: J. Phys Chem., **31**, 1242 (1927).
[47] Lenz: Z. anal. Chem., **22**, 393 (1883).

of blackening after a 30-minute exposure to quartz ultraviolet light of the same intensity. Sodium sulfate and borax likewise have a stabilizing influence. In general, any salt with a readily adsorbed anion will tend to stabilize the sulfide. Nishizawa [48] found that the sulfide was stabilized by glycerol, hydroxides, and the salts and esters of tartaric and polyhydroxystearic acids. The stabilization resulted from the strongly adsorbed anions of these compounds; but this was not understood by Nishizawa.

In addition to its action as an ionizing solvent, water may be assumed to have a purely mechanical effect, forming a film around the liberated zinc, thereby preventing its oxidation by oxygen, ozone, or the liberated sulfur. This effect must be slight, however, since other liquids which wet either zinc or sulfur are without influence on the darkening. Since an excess of water is essential for darkening, it is improbable that the liquid plays a catalytic rôle similar to that in the thermal decomposition of ammonium chloride.[49] Maass and Kempf [34] postulated a reducing action of nascent hydrogen formed by photochemical decomposition of the required water.[50] This assumption seems far fetched since either nascent oxygen [51] or hydrogen peroxide [52] will be formed simultaneously and will neutralize any effect of hydrogen. It was further suggested that formaldehyde,[53] formed by the action of light on moist carbon dioxide, accelerates the reduction. This view is likewise untenable since the blackening goes on in the absence of carbon dioxide.[54] Since Maass and Kempf were the first to suggest that adsorbed zinc ion might sensitize zinc sulfide in the same way that adsorbed silver ion sensitizes silver bromide, one is at a loss to know how they happened to overlook the true rôle of water in the darkening process.

The Decolorization Process

The decolorization of blackened zinc sulfide or lithopone takes place in the dark only in the presence of oxygen or some oxidizing agent such as chlorine, ozone, or hydrogen peroxide. It is obvious, therefore, that the process is only partly reversible if at all, the decolorization in

[48] J. Tokoyo Chem. Soc., **41**, 1054 (1920); Chem. Abstracts, **15**, 1407 (1921); Brit Pat. 156,971 (1919).

[49] Baker: J. Chem. Soc., **65**, 611 (1894).

[50] Berthelot and Gaudechon: Compt. rend., **150**, 1690; **151**, 395 (1910)

[51] Thiele: Ber., **40**, 4914 (1907).

[52] Kernbaum: Compt. rend., **152**, 1668 (1911).

[53] Berthelot and Gaudechon: Compt. rend., **150**, 1169, 1327, 1517, 1690 (1910).

[54] Weiser and Garrison: J. Phys. Chem., **31**, 1239 (1927).

the air being due to the oxidation of the finely divided metal to white zinc oxide or basic carbonate.[6] As already mentioned, Lenard's [38] view is that the photochemical process is reversible. This was based on his observation that a sulfide thrice darkened and allowed to whiten appeared to be as sensitive as the original preparation. Apparently, Lenard started out to prove that the reaction is reversible or he would not have been content with three repetitions. Such a small amount of decomposition takes place that the darkening and decolorization must be repeated a number of times before a marked decrease in sensitivity is noted. Phipson reported that his gatepost, painted with lithopone, became alternately dark in the daytime and white at night for a long time, but at last it remained white. The permanent white color on prolonged aging was probably caused by a protecting film of oxide or basic carbonate. There is apparently no oxidation of the zinc sulfide to zinc sulfate.[55]

Convinced that the photochemical process is reversible, Lenard assumed that discoloration in the presence of oxygen, chlorine, ozone, or hydrogen peroxide is caused by the catalytic action of the oxidizing agent on the recombination of zinc and sulfur. This view is untenable, since it is generally known that zinc reacts more readily with chlorine or ozone than with sulfur. Lenard recognized this condition but got around it by postulating that the zinc atoms which cause the darkening are merely "loosened," whereas we know definitely that the blackening is caused by free zinc.

Prevention of Darkening of Zinc Sulfide Pigments

From a technical standpoint, it is of particular importance to prepare lithopone under such conditions that it is not appreciably discolored by light. From what has been said in the preceding section the following general rules may be deduced: (1) carry out the necessary ignition so that light-sensitive wurtzite is not formed; (2) avoid the presence of soluble zinc salts which increase the light sensitivity; (3) add a salt with a highly adsorbed anion; (4) treat the pigment so as to produce a film of oxide or other light-stable solid around the zinc sulfide particles. A more recent development is the use of small amounts of cobalt salts (p. 293).

Theoretically, the simplest procedure would seem to consist in ignition of the pigment below the temperature where wurtzite is formed.

[55] Wolff: Z. angew. Chem., **37**, 333 (1924).

This is apparently practiced by the New Jersey Zinc Company.[56] It is claimed that the lithopone should be precipitated in the presence of chloride in order to get a commercial product with the desired covering power and oil-adsorbing qualities. Variation in the amount of chloride has a marked influence on the ignition temperature which must be employed to get the desired physical character. But, as already shown, the presence of chloride decreases the stability of the pigment toward light,[57] probably owing to the formation of some soluble zinc chloride during ignition. The addition of 0.005% of cobalt salt to the zinc sulfate solution before treating with barium sulfide is said to prevent the action of chlorine compounds in causing instability.[58] Extended observations disclose that the ignition temperature curves of covering power and oil adsorption on the one hand, and of light stability on the other, cut each other. Hence, to obtain a lithopone that is at once the most light-stable and has the highest covering power, the amount of chloride and the ignition temperature should correspond to the point of intersection of the curves. Thus, for a lithopone precipitated from a zinc sulfate solution (density 1.16) containing not more than 2 g of chlorine per liter, the best ignition temperature is between 700 and 800°. Under these conditions it is probable that the chief product is sphalerite. A rigid control of the ignition temperature is essential for a uniform product.[59] It would seem that the addition of a salt with a strongly adsorbed anion would destroy the light sensitivity resulting from the formation of any wurtzite.

Attention has been called to the spontaneous formation of a protecting film around the sensitive zinc oxide particles by repeated darkening and discoloration in air. It is, of course, impractical to form a protecting film in this way, but most of the earlier methods for obtaining light-proof lithopones involve the addition of an oxidizing agent or some salt that will yield an insoluble protecting film.[6,37,60] More recent recommendations involve a similar principle. For example,

[56] Breyer, Croll, and Farber: U. S Pat. 1,411,645 (1922); Breyer and Farber· 1,446,637 (1923).

[57] Roches: Rev. chim. ind., **31**, 109 (1922); Steinau: Chem.-Ztg., **45**, 741 (1921).

[58] *Cf* Sapgir and Davuidovskaya: J. Chem. Ind. (U.S S R.), No. 3, 44 (1933); Chem Abstracts, **27**, 5557 (1933).

[59] Singmaster, Breyer, and Farber: U. S. Pat. 1,411,646; 1,411,648 (1922)

[60] Alberti: Chem. Zentr., II, 651 (1906); Steinau: I, 1593; Ostwald and Brauer: II, 1707 (1908); Allendorff: I, 116 (1909); Brase. Ger. Pat 254,291 (1909).

Kuzell [61] sprays lithopone in the air to oxidize the zinc sulfide superficially to zinc oxide. Thus, by igniting lithopone so that little wurtzite is formed, or by protecting the light-sensitive sulfide with a strongly adsorbed anion or a non-sensitive film, products are obtained which appear to meet all the technical requirements.

The use of cobalt salts for increasing the light resistance of zinc sulfide pigments calls for special consideration. The author is indebted to Dr. Howard M. Cyr of the New Jersey Zinc Company for the following information:

Jantsch and Wolski [62] pointed out that the presence of a cobalt compound in a zinc sulfide pigment has a beneficial effect on light resistance. The quantity required is given as 0.002 to 0.05% figured as cobalt metal based on the metallic zinc content. In the United States patent the amounts are erroneously specified as 0.02 to 0.5%. Too large quantities are undesirable because of the tinting effect of the cobalt sulfide formed. The cobalt is added preferably as a soluble salt, such as the sulfate, to the zinc liquor, but it is effective also when added to the precipitate before heating. In place of cobalt, salts of nickel, copper, or iron may be used but the quantities of these salts necessary for improvement in the light resistance give sufficient black sulfide to produce noticeable darkening.

X-ray diffraction studies at the New Jersey Zinc Company disclosed that cobalt sulfide formed a solid solution with zinc sulfide. It was observed also that the presence of cobalt decreased the concentration of wurtzite produced under given muffling conditions and, at the same time, decreased the light sensitivity. This is another illustration of correlation between wurtzite content and light sensitivity; but as already pointed out (p. 286), this correlation does not always exist.

By exposing zinc sulfide to light of controlled wave length, it was found that a certain zone in the ultraviolet was most effective in causing darkening, whereas other bands of longer wave length prevented darkening. These two effects usually counterbalanced each other in normal daylight but on certain hazy days the darkening effect predominated.

A comparison of cobalt-treated zinc sulfide pigments with the untreated pigments disclosed that the rate of darkening of both was the same. On the other hand, the rate of bleaching was found to be greatly accelerated by the presence of the cobalt compound. Since cobalt is a

[61] U. S. Pat. 1,399,500 (1922); *cf., also,* Nishizawa: J. Tokoyo Chem. Soc., **41**, 1054 (1920); Brit. Pat. 156,971 (1921).

[62] Ger. Pat. 435,840 (1923); U. S. Pat. 1,693,902 (1924).

good oxidation catalyst, its acceleration of bleaching is in agreement with the theory that the bleaching process consists of a reoxidation of metallic zinc.

The addition of cobalt to lithopone according to Jantsch and Wolski's patent is used by many producers of the product in this country and in Europe.

CADMIUM SULFIDE PIGMENTS

Cadmium sulfide is used under conditions where the cheaper, bright yellows are not satisfactory.[63] Its main uses are in the coloring of vulcanized rubber, as a brilliant artists' color, and for switch and target enamels. It is unaffected by exposure to light, heat, and city atmospheres and mixes easily with any paint vehicle.

Formation

The yellow sulfide called "cadmium yellow" is obtained by precipitating cold solutions of low cadmium content with hydrogen sulfide or by precipitating cadmium solutions with the alkali sulfides. The deep orange pigment known as "cadmium orange" is precipitated from hot strongly acid solutions with hydrogen sulfide or by long boiling of cadmium solutions with sodium thiosulfate or alkali sulfide. Richards and Roepper[64] have patented processes for preparing cadmium yellow by electrolysis of sodium thiosulfate solution with a cadmium anode and an indifferent cathode, and by alternating-current electrolysis of thiosulfate solution with cadmium electrodes. The latter process is too inefficient to be of value,[65] but the former has been improved to the point where it may find some technical application. Fischer[66] substituted for the indifferent cathode one consisting of a mixture of equal parts of sulfur and copper sulfide, which has a relatively low resistance; the current efficiency of Fischer's process is 100%. At a current density of 0.05 ampere/cm^2, both yellow and orange sulfide are formed; and at 0.005 ampere/cm^2, only the yellow is obtained. Fink and Grosvenor[67] used sodium sulfide as the electrolyte with cadmium stick anode and iron cathode surrounded by ferrous sulfide as the source of sulfur. Sacher[68] questions the applicability of the electro-

[63] Toch: "Chemistry and Technology of Mixed Paints," 73 (1925); *cf.* Bugden: Continental Met. & Chem. Eng., **2**, 109 (1927).

[64] Richards: Trans. Am. Electrochem. Soc., **1**, 221 (1902).

[65] White: Trans. Am. Electrochem Soc., **9**, 305 (1906).

[66] Z. Elektrochem., **31**, 285 (1925); Lorenz: Z. anorg. Chem., **12**, 442 (1896).

[67] Trans. Am. Electrochem. Soc., **58**, 475 (1930).

[68] Farbe u. Lack, 246 (1931).

lytic method as compared with the batch precipitation method for technical manufacture.

A very satisfactory cadmium lithopone or cadmipone [69] may be prepared by the interaction of cadmium sulfate and barium sulfide.

Color

The variation in color of the pigment was attributed to adsorbed impurities by Follenius [70] and to the existence of allotropic modifications of different density and crystal structure by Buchner [71] and Klobukow.[72] Microscopic examination of pigments of various colors led Allen, Crenshaw, and Merwin [73, 74] to conclude that there is but one crystalline form, the color variation being caused by difference in the size and physical character of the particles. In accord with this view Müller and Löffler [75] obtained products which gave the same x-radiogram but which varied in color from yellow to red by precipitating cadmium sulfate solutions with hydrogen sulfide in the presence of different amounts of sulfuric acid. The crystal structure of Muller and Löffler's colloidal preparations was cubic, whereas that of Allen, Crenshaw, and Merwin's microscopic preparations, formed by digestion at elevated temperatures, was hexagonal like the mineral greenockite.

From the above considerations it would follow that both crystalline forms may be either yellow or red depending on the particle size. The question is whether the colloidal, precipitated forms are always cubic in structure. This was settled by Milligan,[76] who precipitated various cadmium salts at 30 and 100° with and without the addition of the corresponding acids, noted the color of the resulting products, and determined the crystal structure of each by x-ray analysis. The results which are given in Table XXXV show conclusively that either the cubic or hexagonal modifications may be yellow or red (or orange), depending on the conditions of formation and treatment. All samples appear more or less orange upon grinding the dry aggregates to a powder. The cubic form is usually obtained from sulfate or nitrate solution, especially from hot or acid solutions; the hexagonal modification is

[69] Ward: J. Oil and Colour Chem. Assoc., **10**, 4 (1927).
[70] Z. anal. Chem., **13**, 417 (1874).
[71] Chem.-Ztg., **11**, 1087, 1107 (1887).
[72] J. prakt. Chem., (2) **39**, 414 (1889).
[73] Allen, Crenshaw, and Merwin: Am. J. Sci., (4) **34**, 341 (1912).
[74] *Cf., however,* Egerton and Raleigh: J. Chem. Soc., **123**, 3019 (1923).
[75] Z. angew. Chem., **46**, 538 (1933).
[76] J. Phys. Chem., **38**, 797 (1934).

TABLE XXXV

COLOR AND CRYSTALLINE FORM OF PRECIPITATED CADMIUM SULFIDE

Cadmium salt used 0.1 *N*	Without the addition of acid				In the presence of added acid			
	At 30°		At 100°		At 30°		At 100°	
	Color	Crystalline form	Color	Crystalline form	Color	Crystalline form	Color	Crystalline form
Sulfate	Yellow	Hexagonal*	Yellow	Cubic	Yellow	Cubic†	Red	Cubic
Nitrate	Yellow	Hexagonal	Yellow	Hexagonal*	Yellow	Cubic†	Red	Cubic
Chloride	Yellow	Hexagonal*	Yellow	Hexagonal	Yellow	Hexagonal	Red	Hexagonal
Bromide	Yellow	Hexagonal*	Yellow	Hexagonal	Orange	Hexagonal	Red	Hexagonal
Iodide	Orange	Hexagonal	Orange	Hexagonal	Orange	Hexagonal	Orange	Hexagonal

* Trace of cubic β-cadmium sulfide.
† Trace of hexagonal α-cadmium sulfide.

usually thrown down from chloride, bromide, or iodide solutions. Small amounts of the cubic form sometimes occur in essentially hexagonal precipitates; this is probably more or less accidental, depending upon slight variations in the conditions of precipitation. The variation in color must be attributed to differences in the physical character of the precipitate such as particle size, the nature of the surface of the particles, and the state of aggregation. Difference in particle size alone will not suffice to explain all the known facts, since large crystals of greenockite are yellow, although red (or orange) particles are usually larger and more granular than yellow ones. The view that color variations result chiefly from differences in physical character of the samples is in agreement with the observation that the red particles obtained from hot acid solutions possess less adsorptive capacity than the yellow particles formed in the cold (p. 257).

In discussing the cause of differences in color, it must be borne in mind that, in the last analysis, the actual color is determined by the relative amounts of light transmitted and reflected.[73] For example, greenockite absorbs all the blue and part of the green of the spectrum and transmits the remainder. When the grains are in masses having diameters of 0.2 to 1.0 mm and are bounded by bright faces, a large amount of blue light is reflected directly by resonance and small amounts of red, orange, yellow, and green are reflected after passing through the surface layer of the crystals. The combined effect of all the reflected light is a lustrous dark yellow to yellowish green. Similarly, plane-faced bright crystals having diameters of but 0.01 mm or less reflect about the same amount of blue by resonance but they re-

flect much more of the light which penetrates the surface, the resulting color being a pure yellow. A mass of crystals of the same size with dull faces have a light yellow-brown color. The grains of powdered crystals usually have bright but not plane surfaces and give a brilliant orange color, for there is less direct reflection and much of the light finally reflected from the interior has penetrated deeper and thus lost more green and yellow than a powder having plane-faced fragments.

With the extremely minute submicroscopically crystalline or amorphous particles, there is more absorption in the yellow and green and, by transmitted light, the color appears orange-yellow in films 0.01 mm thick. A powder with grains 0.0001 to 0.001 mm in diameter is bright yellow with a tinge of orange, and one with grains 0.004 to 0.007 mm in diameter, or compact aggregates of smaller granules, is bright orange.

VERMILION

Vermilion is the synthetic red hexagonal modification of mercuric sulfide which corresponds to the mineral cinnabar. The native product does not make a satisfactory pigment, for the impurities dull the color and it does not possess the desired physical character. The pigment is synthesized by dry and wet processes. The former, which is used most frequently, consists essentially in the formation of the black sulfide by direct union of mercury and sulfur, and its subsequent conversion into the red variety by a process of sublimation. Two dry processes are generally recognized: the Dutch and the Chinese.[77] The product prepared by the Chinese process is celebrated for its fine color which inclines to a carmine. At one time it was thought that the Chinese employed a wet method, but this was not the case.[78] The Dutch and Chinese processes are essentially the same, any differences in physical character or color resulting from the care exercised in the sublimation process.

The wet process depends on the fact that alkali and ammonium sulfides and polysulfides dissolve the black sulfide which subsequently precipitates as the less soluble red form.[79] Rise in temperature and excess sulfur favor the process.[80] The most satisfactory method of

[77] Hurst and Heaton: "A Manual of Painters' Colors, Oils, and Varnishes," 5th ed, 163 (1913).

[78] Chem. News, **50**, 77 (1884); J Soc. Chem. Ind., **1**, 95 (1882).

[79] Brunner: Pogg Ann., **15**, 593 (1829); Firmenich: Dinglers Polytech. J., **172**, 370 (1864).

[80] Stanek: Z. anorg. Chem., **17**, 117 (1898); Christy: Am. J. Sci., (3) **17**, 453 (1879); Ippen: Z. Krist., **27**, 110 (1897).

preparation is to heat the black sulfide at 100° in a closed vessel.[81] The black modification is more readily soluble in concentrated sodium or potassium sulfide than in ammonium sulfide. The pigment prepared with alkali sulfide in the presence of excess mercuric salt is much darker than the vermilion powder formed with ammonium sulfide. The dark product consists of crystals sufficiently large to be easily recognized by the naked eye. When the larger crystals are ground up fine, the color is scarcely distinguishable from the ammonium sulfide preparation.

It is difficult to remove completely the adsorbed sulfide and sulfur from vermilion prepared in the wet way, and these impurities are detrimental to the product. For this reason, Picton and Linder [82] heated the sol in a closed vessel from 160 to 170° for several hours until the desired shade of red was produced. Instead of starting with the black sulfide, Liebig [83] heated freshly prepared infusible white precipitate, NH_2HgCl, with ammonium polysulfide at 45°; and Hausamann [84] heated a solution of the white precipitate in concentrated sodium thiosulfate.

In addition to its use as a pigment in paint, vermilion is employed in making Chinese red ink and for coloring porcelain, paper, candles, etc. Most of the numerous temples throughout China are painted red with vermilion, since the Chinese look upon this as a lucky color.

ARSENIC SULFIDE PIGMENTS

Two arsenic compounds, the trisulfide As_2S_3 and the disulfide As_2S_2, have been used as pigments. The trisulfide known as King's yellow is a brilliant but fugitive and extremely poisonous pigment which was extensively used before the introduction of the similarly colored lead and barium chromate. The pigment is prepared by precipitation from an arsenious acid solution with hydrogen sulfide or by subliming a mixture of arsenic trioxide and sulfur. The sulfide is found native as the mineral orpiment which is sometimes ground and used as a pigment.

The disulfide occurs in nature as the mineral realgar. The commercial red arsenic glass or ruby sulfur is an artificial disulfide prepared by mixing arsenical pyrites and common pyrites in such propor-

[81] Allen, Crenshaw, and Merwin: Am. J. Sci., (4) **34**, 367 (1912).
[82] Brit. Pat. 5,120 (1892).
[83] Ann, **5**, 239; **7**, 49 (1833).
[84] Ber., **7**, 1747 (1874).

tion that the mixture contains about 15% of arsenic and 27% of sulfur. Such a mixture is then sublimed and the resulting product is melted with sulfur to give it the proper color. This so-called ruby sulfur is a red glassy mass consisting of arsenic disulfide and sulfur in varying amounts.[85] It was formerly used as an orange pigment, but, like the trisulfide, it is no longer employed to any extent.

ANTIMONY SULFIDE PIGMENTS

Antimony Trisulfides

Classification. Antimony trisulfide pigments are usually divided into two classes: the natural and the artificially prepared varieties. The first class includes black crystalline stibnite and a brick-red trisulfide called metastibnite which is said to be amorphous;[86] the second class includes the precipitated sulfides which are sometimes used as pigments. The precipitated trisulfides have been classified into two subgroups: those thrown down in the presence, and those thrown down in the absence, of hydrogen sulfide. The first group includes the trisulfides precipitated by hydrogen sulfide directly and by the action of acids on the antimonates and thioantimonates. The color is usually some shade of orange, and the group may be designated as the "antimony oranges." The pigments are sometimes called the "antimony goldens," but the former term is preferable since antimony pentasulfide is called the golden sulfide of antimony. The second group of trisulfides is formed by the interaction of an antimonous salt and sodium thiosulfate.[87] The color is usually some shade of red, and the group may be designated the "antimony crimsons."

Factors Influencing the Color. Currie[88] made an extended study of the various factors influencing the color of antimony sulfide pigments. The interaction of dilute solutions of sodium thiosulfate and antimony trichloride at room temperature gives a light yellow precipitate which yields a fine yellow powder when washed and dried in vacuum. On heating at 100 to 110° in a hot-air oven, the color changes steadily through various shades of orange to a uniform red and finally to a rich crimson. Raising the temperature to 150 to 170° causes the color to change through a series of crimson shades to maroon, finally becoming uniformly black. The presence of salts, chlorides especially,

[85] Roscoe and Schorlemmer: "Treatise on Chemistry," 5th ed., **1**, 708 (1920).
[86] Becker: Proc. Am. Phil. Soc., **25**, 168 (1888).
[87] *Cf.* Long: J. Am. Chem. Soc., **18**, 342 (1896).
[88] J. Phys. Chem., **30**, 223 (1926).

and of acids, lowers the temperature at which the change to the black modification is complete.[89] In the presence of 9 *N* HCl, the transformation at the boiling point takes place quite rapidly;[90] but the process goes on slowly even at room temperature. Two grams of the orange compound in 5-cc portions of 12 *N*, 7 *N*, and *N* HCl are transformed completely into the black crystals in 0.5 day, 1 day, and 10.5 days, respectively; phosphoric, acetic, and sulfuric acids have little effect within two months.[91] A 0.5-g sample of the orange sulfide in contact with water was found by Lehrman [92] to change completely to black in 10 months. Anions hasten the change in the order: $S > water > NO_3 > Cl > SO_4 > C_2H_3O_2$; and cations in the order: $H > water > Na > NH_4$.

The wide variation in color from yellow through orange, crimson, and maroon to black may be due entirely to variation in the size of the particles, the larger particles possessing the darker shades. Since sulfides tend to give negatively charged sols, the pigments formed in the presence of readily adsorbed anions are more highly peptized and hence are lighter in color than those precipitated in the presence of strongly adsorbed cations which favor coagulation into denser aggregates possessing a darker color. Moreover, the particles precipitated in the presence of gelatin are smaller and lighter in color than those obtained under similar conditions in the absence of a protecting colloid.

Antimony Crimsons. The yellow and crimson trisulfides appear to be amorphous to x-rays, but the final black product has a crystalline structure identical with the natural stibnite. The maroon shades are intimate mixtures of crimson with black sulfide; various maroons can be synthesized by mixing the black and crimson powders. The densities of the sulfides change in exactly the same order as the colors: the yellow pigments have a density of approximately 4.10 to 4.12; the crimson, 4.12 to 4 38; and the black, 4.6 to 4.8.[93] The density of the maroon shades is usually about 4.4 to 4.5; the approximate density may be calculated by comparing the color of the maroon pigment with a mixture of known amounts of crimson and black sulfides of known density.

Stibnite and the artificial black sulfides are formed under condi-

[89] De Bacho: Ann. chim. applicata, **12**, 143 (1919).

[90] Mitchell: Chem. News, **67**, 291 (1893).

[91] Wilson and McCrosky: J. Am. Chem. Soc., **43**, 2178 (1921).

[92] J. Phys. Chem., **35**, 2763 (1931).

[93] Currie: J. Phys. Chem., **30**, 232 (1926); *cf.* Kirchhof: Z. anorg. Chem., **114**, 266 (1920).

tions which would give relatively large crystals. Currie disintegrated stibnite in an electric arc under water according to Svedberg's method, obtaining a sludge of finely divided yellow crystalline particles. The fact that the crystalline sulfide may be either yellow or black, depending on the size of the particles, supports Berthelot's[94] contention that the transformation from one color to another involves no measurable heat effect. Currie was unable to prepare a crystalline crimson pigment, the larger particles of amorphous trisulfide alone giving the crimson color. It is possible, however, that the natural red meta-stibnite which is said to be amorphous would prove to be crystalline if examined with x-rays.

Antimony Oranges. The trisulfides, as ordinarily precipitated by hydrogen sulfide from a solution of trivalent antimony, are light golden yellow and may be dried in vacuum to give a rich golden color. Unlike the "antimony crimsons," heating to 105 to 110° causes little or no change in color whereas further heating to 150 to 170° causes the pigment to change through varying shades of brown to the black modification without showing any signs of the crimson color. The brown colors were found to be mixtures of amorphous golden with crystalline black trisulfide in varying proportions. Darkening through the crimson and maroon shades is prevented by adsorption of hydrogen sulfide on the surface of the golden particles which keeps them from coming into intimate contact and coalescing to the darker shades before the transformation to the black crystals takes place.

Both the orange and crimson trisulfide possess good hiding power and mix well with oil. They cannot, of course, be employed with alkaline vehicles, but they are quite stable in light and in the air. Crimson antimony is the most valuable red pigment employed in coloring rubber.[95]

The Golden Sulfide of Antimony

The term golden sulfide of antimony is frequently applied to antimony pentasulfide, but, as we have seen (p. 227), it is usually a solid solution of the tetrasulfide and sulfur. In general, the influence of temperature in the neighborhood of 100° on the golden sulfide is slight, a uniform darkening being the most noticeable effect. Above 115°, however, the tetrasulfide decomposes rapidly to trisulfide and sulfur,

[94] Compt. rend., **139**, 97 (1904); *cf., however,* Guinchant and Chrétien: **139**, 51 (1904).

[95] *Cf.* Bierer: Chem. Age (N. Y.), **28**, 194 (1920).

further heating producing color changes like those of all trisulfides precipitated in the presence of hydrogen sulfide.

Golden sulfide of antimony is a valued pigment for rubber goods, and a number of patents have been granted for its commercial production.[96] In the rubber industry "golden sulfide" is applied to a fairly wide range of products varying in shade from a golden yellow to a deep orange and in composition from a nearly pure antimony trisulfide to a mixture containing a relatively high percentage of tetrasulfide.[97] In addition to its value as a pigment, antimony sulfide is superior to iron oxide pigment as a compounding ingredient. Mixes[98] in which antimony sulfide is used possess strength and aging qualities[99] superior to similar mixes containing iron oxide.

MOSAIC GOLD

Mosaic gold is the name given to the pigment stannic sulfide which was extensively used in the eighteenth century as a gold coloring matter in paints. It was prepared then, as now, by subliming a mixture of tin amalgam, sulfur, and ammonium chloride. For example, on heating 18 parts of tin amalgam containing 6 parts of mercury with 6 parts of ammonium chloride and 7 parts of sulfur, the ammonium chloride, mercuric chloride, and stannous chloride sublime, leaving the pigment stannic sulfide in the form of beautiful golden yellow translucent scales.[100] At the present time it is employed as a bronzing powder for wood, metal, wallpaper, and gypsum plaster.

[96] *E.g*, Chaillaux: Brit. Pat. 151,422 (1919); Stark: U. S. Pat. 1,414,836; 1,415,127 (1922); Bezzenberger: 1,528,394 (1925); Wilson: Can. Pat. 252,563 (1925).

[97] *Cf.* Luff and Porritt: J. Soc. Chem. Ind., **40**, 275*T* (1921).

[98] The term "mixing" is applied to the operation by which sulfur and other materials are incorporated with rubber.

[99] Anderson and Ames: J. Soc. Chem. Ind., **42**, 136*T* (1923); Woodward: Rubber Age, **1**, 99 (1917).

[100] Woulfe: Phil. Trans., **61**, 114 (1771).

PART IV

THE COLLOIDAL FERROCYANIDES AND FERRICYANIDES

CHAPTER XVI

COLLOIDAL FERROCYANIDES AND FERRICYANIDES: GENERAL PROPERTIES

The interaction of dilute solutions of metallic salts and alkali or alkaline-earth ferro- and ferricyanides gives precipitates that vary in physical character from highly gelatinous to flocculent; with concentrated solutions jellies result. The highly hydrous gels adsorb the common anions so strongly that the precipitates are always contaminated with the corresponding alkali or alkaline-earth salts, especially when the precipitation is accomplished with an excess of the latter. In some instances definite double salts are formed, but because of their high adsorption capacity they are seldom pure.

HEAVY-METAL FERROCYANIDES

Adsorption of Water

The metallic ferrocyanides are frequently assigned formulas which suggest that they form definite hydrates. Copper ferrocyanide, for example, is said to contain 10[1] molecules of water when in equilibrium with 5% H_2SO_4; 7,[2] when air dried; and 6[1] or 3[3] when dried over concentrated H_2SO_4. Löwenstein[4] showed, however, that a preparation containing 10 molecules of water at 25° loses water continuously without the formation of a definite hydrate.[5] Similarly, zinc ferrocyanide has been assigned 3,[6] 4,[7] 5,[8] 6,[9] and 7[2] molecules of water when

[1] Wyrouboff: Ann. chim. phys., (5) **8**, 444 (1876); Löwenstein: Z. anorg. Chem., **63**, 125 (1909).

[2] Rammelsberg: Pogg. Ann., **73**, 80 (1848).

[3] Hartung: Trans. Faraday Soc., **15** (3), 160 (1920); *cf., also,* Tinker: Proc. Roy. Soc. (London), **93A**, 268 (1917).

[4] Z. anorg. Chem., **63**, 125 (1909).

[5] *Cf., also,* Katz: Koninkl. Akad. Wetenschappen, Amsterdam, Verst., **31**, 542 (1923).

[6] Schindler: Phil. Mag., **35**, 71 (1810).

[7] Miller: J. Am. Chem. Soc., **18**, 1100 (1896).

[8] Cumming and Good: J. Chem. Soc., 1924 (1926).

[9] Luckow: Chem.-Ztg., **16**, 836 (1892).

dried under varying conditions; but Löwenstein showed that the gel loses all its water continuously in the presence of 97% H_2SO_4. In the light of these typical results, one should be slow to accept the formulas for the alleged hydrates of the metallic ferrocyanides. It is altogether likely that some of them form definite hydrates under certain conditions, but in every instance their acceptance should be based on a phase-rule study of the ferrocyanide-water system and not on an analysis of a product prepared and dried in a special way.

Adsorption of Ferrocyanide Ion

The strong adsorption of ferrocyanide ions by ferrocyanide gels is well illustrated by the taking up of potassium, sodium, and hydrogen ferrocyanides by copper ferrocyanide.[10] Solutions of the ferrocyanides and cupric chloride were prepared such that 50 cc of the former were exactly equivalent to 100 cc of the latter, and, on mixing the respective amounts, theoretically 0.5 g of $Cu_2Fe(CN)_6$ was formed. To portions of the copper chloride solution were added varying amounts of the ferrocyanides in a total volume of 250 cc, and after standing 24 hours the supernatant solutions were analyzed for excess ferrocyanide. A typical set of observations is given in Table XXXVI, and all the data

TABLE XXXVI

CARRYING DOWN OF $K_4Fe(CN)_6$ BY $Cu_2Fe(CN)_6$

Cc solutions mixed (in 250 cc)		Equilibrium concentration $K_4Fe(CN)_6$ millimols/l	$K_4Fe(CN)_6$ carried down mol/mol $Cu_2Fe(CN)_6$
$CuCl_2$	$K_4Fe(CN)_6$		
100	50	0 0	0 000
100	60	0 0	0 200
100	70	0 0	0 400
100	75	0 069	0 478
100	80	0 231	0 560
100	90	0 949	0 638
100	100	1 924	0 673
100	140	6 271	0 736
100	140*	22 076	0 855

* Double the concentration of previous solution.

[10] Weiser: J. Phys. Chem., **34**, 335 (1930); Müller, Wegelin, and Kellerhoff: J. prakt. Chem., (2) **86**, 82 (1912).

are shown graphically in Fig. 45. These results show the marked tendency of the freshly formed gel to carry down ferrocyanides, especially the potassium and sodium salts. Indeed, this tendency is so great that copper is present in the supernatant solution when equivalent amounts of copper and alkali ferrocyanides are mixed. With

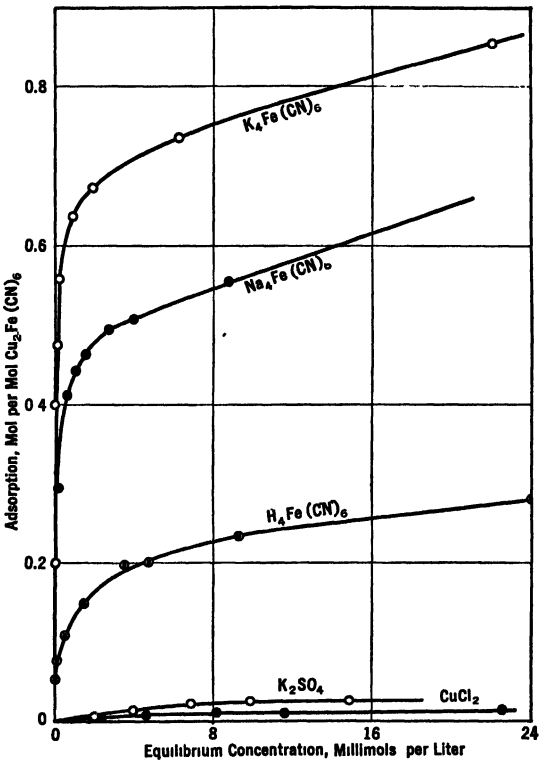


FIG. 45.—Adsorption of ions by copper ferrocyanide gel.

hydroferrocyanic acid, on the other hand, pure $Cu_2Fe(CN)_6$ is obtained by mixing equivalent solutions.

Recognizing the alkali impurity in copper ferrocyanide gels, Duclaux suggests that they should be represented by the general formula $Cu_mK_nFe(CN)_6$, where $m + n/2 = 2$. He believes that potassium ferrocyanide combines with the copper salt to form a series of double salts; but the evidence for this point of view is inconclusive. It seems

just as likely that the gel is copper ferrocyanide with potassium ferrocyanide adsorbed in varying amounts depending on the relative concentrations of the salts and the conditions of precipitation. This does not preclude the formation of definite double salts under certain conditions; but the composition of the precipitated gel can be varied continuously over such a wide range that one is not justified in concluding that a double salt is formed simply from the analysis of an amorphous mass.

From the curve in Fig. 45, it might be argued that a definite double salt is formed of some such composition as $5Cu_2Fe(CN)_6 \cdot 2K_4Fe(CN)_6$ and that the upper portion of the curve represents the adsorption of $K_4Fe(CN)_6$ by the double salt. Although this is possible, the available evidence is inadequate to establish the existence of a definite double salt of this formula. Fordham and Tyson [11] obtained a characteristic electron diffraction pattern for copper ferrocyanide membranes prepared by the interaction of copper sulfide and potassium ferrocyanide. This proves that the precipitate is definitely crystalline but it does not establish whether the precipitate is copper ferrocyanide or a double salt. Milligan in the author's laboratory, had previously secured an x-ray diffraction pattern for the gel which was found to correspond essentially to the electron diffraction pattern of Fordham and Tyson. A systematic study by analytical, x-ray, and electron diffraction methods of the gels formed under various conditions will be necessary to establish their composition (p. 310). Numerous definitely crystalline alkali and alkaline-earth cupric ferrocyanides have been described; [12] but the only ones Messner [13] was able to prepare have the simple formula $X_2{+}CuFe(CN)_6$, where $X+ = K$, Na, and NH_4, or $X{+}{+}CuFe(CN)_6$ where $X{+}{+}$ = Mg, Ca, Sr, and Ba.

Titration of Ferrocyanide Solutions

Procedure and General Results. Attempts have been made to determine the composition of the precipitated ferrocyanide gels by electrometric [14] and conductometric [15] titration. The most recent work of

[11] J. Chem. Soc., 483 (1937).

[12] *Cf.* Bolley: Ann., **106**, 228 (1858); Wonfor: Jahresber., 233 (1862); Wyrouboff: Ann. chim. phys., (5) **8**, 444 (1876).

[13] Z. anorg. Chem., **8**, 368 (1895).

[14] Bichowsky: Ind. Eng. Chem., **9**, 668 (1917); Treadwell and Weiss: Helv. Chim. Acta, **2**, 680 (1919); Treadwell and Chervet: **5**, 633 (1922); **6**, 550 (1923).

[15] Kolthoff: Z. anal. Chem., **62**, 209 (1923); Kolthoff and Verzijl: Rec. trav. chim., **43**, 394 (1924); *cf.* Ibarz and Feyto: Anales soc. españ. fís. quím., **34**, 823 (1936).

this kind was done by Britton and Dodd,[16] who made conductivity measurements at 25° on mixtures of heavy-metal salts and potassium ferrocyanide: first, in the form of direct conductometric titration of 125 cc of 0.02 *M* salts with 0.1 *M* $K_4Fe(CN)_6$; and second, on similar mixtures of reactants after they had stood in a thermostat until equilibrium was set up. In Fig. 46 are given the curves constructed from

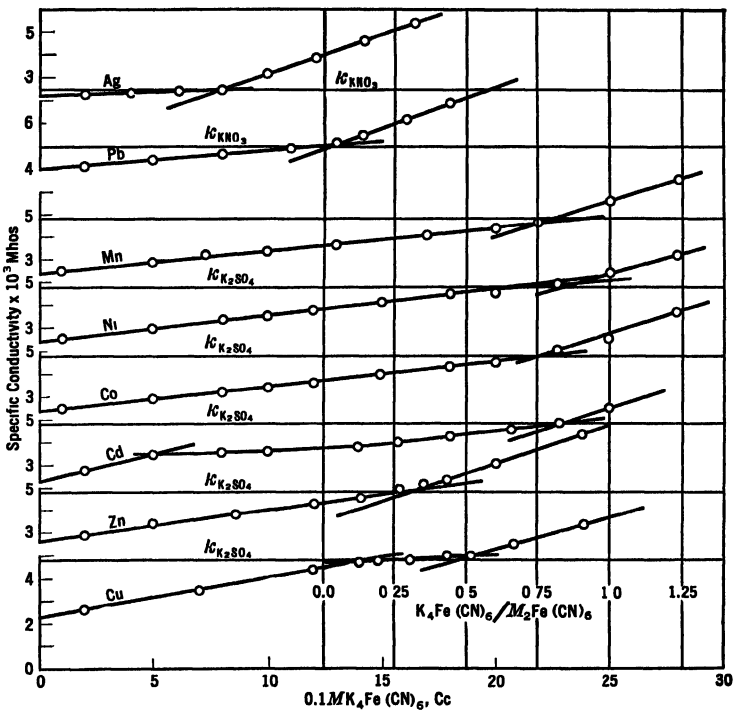


FIG 46.—Titration curves for ferrocyanide solution with various metallic salts.

data corresponding to equilibrium conditions and the horizontal lines which represent the specific conductivity of potassium sulfate formed as a result of the equation: $2MSO_4 + (1 + X)K_4Fe(CN)_6 \rightarrow M_2Fe(CN)_6 \cdot XK_4Fe(CN)_6 + 2K_2SO_4$.

The values of $X[= K_4Fe(CN)_6]$ deduced from the conductivity data, and from analysis of the precipitates formed in the presence of

[16] J. Chem. Soc., 1543 (1933).

varying excess of potassium ferrocyanide, are summarized in Table XXXVII. The direct analysis of the precipitates is of little use in

TABLE XXXVII

POTASSIUM FERROCYANIDE IN FERROCYANIDE GELS

[X = mol $K_4Fe(CN)_6$ per mol $M_2Fe(CN)_6$]

M	From conductivity measurements				From analysis of gel
	First break		Second break		
	Cc 0 1 M $K_4Fe(CN)_6$	X	Cc 0 1 M $K_4Fe(CN)_6$	X	X
Cu	14	0 12	18 7	0 52	0 52–0 71
Zn	..		16 4	0 31	0 71–0 78
Cd	.	.	23 0	0 84	0 59–0 90
Co	.	..	22 3	0 78	0 50–0 74
Ni	19.7	0 58	23 4	0 87	0 56–1 22
Mn	...	..	23 0	0.84	0 83–0 92
Pb	12 5	0 0	.. .		very small
Ag	8 3	0 33		.. .	0 33

estimating the exact composition since they are peptized before they can be washed free from entrained salt. Hence the values in the last column of the table represent only very rough approximations.

Copper Ferrocyanide. In the titration of copper sulfate, normal cupric ferrocyanide with a little adsorbed copper sulfate was obtained whenever the precipitation was accomplished in the presence of excess copper. When precipitation of copper is complete the composition of the precipitate is $Cu_2Fe(CN)_6 \cdot 0.12K_4Fe(CN)_6$. Further addition of ferrocyanide causes no appreciable change in the conductivity, indicating that all the ferrocyanide is taken up until the composition is $Cu_2Fe(CN)_6 \cdot 0.4\text{–}0.5K_4Fe(CN)_6$. Thereafter some ferrocyanide remains in the solution and the conductivity rises. These results confirm the findings of Weiser shown in Fig. 45; but neither series of experiments establishes the formation of a definite double salt. Britton and Dodd are inclined to believe that the second break in their conductivity curve indicates the formation of a compound $2Cu_2Fe(CN)_6 \cdot K_4Fe(CN)_6$ which adsorbs ferrocyanide strongly; but, since copper ferrocyanide gel adsorbs potassium ferrocyanide so strongly, the value of $X = 0.52$ at the second break cannot all be combined ferrocyanide.

The value of X (combined) might be 0.4, giving a compound $5Cu_2Fe(CN)_6 \cdot 2K_4Fe(CN)_6$, with adsorbed $K_4Fe(CN)_6$, but as already pointed out the experimental evidence is hardly sufficient to justify this conclusion.

Zinc Ferrocyanide. The compound $Zn_2Fe(CN)_6$, like the corresponding copper salt, results by precipitation with zinc ion in excess or by the interaction of equivalent amounts of zinc ion and hydroferrocyanic acid. Zinc may be estimated volumetrically by titration with potassium ferrocyanide in neutral or acid solution. The following reaction is said to take place: $2K_4Fe(CN)_6 + 3Zn^{++} \rightarrow K_2Zn_3[Fe(CN)_6]_2 + 6K^+$, with the formation of a definite double salt. Referring to Table XXXVII it will be seen that the observed equilibrium concentration of $K_4Fe(CN)_6$ at the break in the curve is less than corresponds to the above formula. In the rapid conductometric titration, the break was observed at a point corresponding to the formula. This indicates that the precipitate is not a definite salt of the above composition but is either zinc ferrocyanide with adsorbed potassium ferrocyanide or a double salt containing less potassium ferrocyanide than the above, together with adsorbed potassium ferrocyanide. To take care of possible variations in the composition of the precipitated gel and so to obtain accurate results in the estimation of zinc, it is essential not only that the conditions be rigidly controlled but also that they be exactly the same as in the standardization of the ferrocyanide solution against zinc.

Zinc may be estimated by potentiometric titration[17] with potassium ferrocyanide in the absence of much sodium, rubidium, cesium, ammonium, magnesium, calcium, copper, cadmium, manganese, and iron. At the end point the zinc is all precipitated as the alleged double salt $K_2Zn_3[Fe(CN)_6]_2$.

Uranium Ferrocyanide. Tetravalent uranium gives a red precipitate of $UO_2Fe(CN)_6$. If alkali ferrocyanide is in excess a sol is formed which is useful in the colorimetric determination of small amounts of uranium.[18] Potentiometric titrations of uranyl nitrate and acetate with potassium ferrocyanide indicate that the normal salt is obtained with the acetate and a potassium uranyl double salt with the nitrate.[19]

[17] Bichowsky: Ind. Eng. Chem., **9**, 668 (1917); Treadwell and Weiss: Helv. Chim. Acta, **2**, 694 (1919); Kolthoff: Rec. trav. chim., **41**, 425 (1922); Kolthoff and Verzijl: **43**, 380 (1924); Z. anorg. Chem., **132**, 318 (1923); Müller: **128**, 125 (1923); Saito: Chem. Abstracts, **24**, 1595 (1930); **25**, 4480, 5860 (1931).

[18] *Cf.* Tissier and Bénard: Compt. rend. soc. biol., **99**, 1144 (1928).

[19] Atanasiu: Bul. Chim. Soc. Română, Stiinte, **30**, 77 (1927).

Lead Ferrocyanide. Unlike the gelatinous ferrocyanide of copper, zinc, cadmium, cobalt, nickel, manganese, and uranyl, lead ferrocyanide is more granular, adsorbs little potassium ferrocyanide, and forms no double salts.[20] The precipitate gives an electron diffraction pattern indicating that it consists of simple cubic crystals larger than 200 Å in length.[11] The reaction between lead and ferrocyanide ions may be used for the conductometric or potentiometric estimation of lead; and for the titrometric determination of ferrocyanide ions using sodium alizarin sulfonate as an adsorption indicator (p. 132).[21]

Silver Ferrocyanide. The precipitate appears to come down first as $Ag_4Fe(CN)_6$,[22] going over rapidly and completely into insoluble $KAg_3Fe(CN)_6$ [23] with the required excess of potassium ferrocyanide.

In conclusion it appears that the normal heavy-metal ferrocyanides may be prepared pure by adding solutions of alkali or alkaline-earth ferrocyanides to an excess of a solution of heavy-metal salt or by dissolving the hydroxides or carbonates of the metals in hydroferrocyanic acid. With excess soluble ferrocyanide the gels are always contaminated by adsorbed ferrocyanide, but, under suitable conditions, definite double salts may be formed. As a rule it is impossible to decide, on the basis of existing evidence, whether a given gel is an adsorption complex or a definite double salt. The only hope of settling this question, with highly adsorptive gelatinous precipitates, rests on whether the gels formed under varying conditions are crystalline to x-rays and so lend themselves to x-ray analysis.

Rhythmic Precipitation

By allowing alkali ferro- and ferricyanide solutions to diffuse into jellies containing heavy-metal salts, most of the common ferro- and ferricyanides have been precipitated in the form of rhythmic bands. Holmes [24] obtained copper ferrocyanide in silica; Dounin and Schemjakin,[25] copper and silver ferrocyanides in agar; and Chatterji and Dhar,[26] the ferro- and ferricyanides given in Table XXXVIII. Two

[20] *Cf., also,* Kolthoff: Z. anal. Chem., **62,** 211 (1923); Müller and Kogert: **75,** 237 (1928).

[21] Burstein: J. Russ. Phys.-Chem. Soc., **59,** 521 (1927).

[22] Kolthoff: Z. anal. Chem., **62,** 210 (1923); Kameyama and Gorai · J Soc. Chem. Ind., Japan (Suppl.), **30,** 6*B* (1927).

[23] Steyer: Z. anal. Chem, **74,** 108 (1928); Budnikov: **73,** 433 (1928)

[24] J. Am. Chem. Soc., **40,** 1187 (1918).

[25] Kolloid-Z., **47,** 335 (1929).

[26] Kolloid-Z., **40,** 97 (1926).

types of rings were observed: type I rings were sharp with precipitate-free spaces between; and type II were alternate layers of coagulated and colloidally dispersed salt. By decreasing the concentration of diffusing electrolytes, the number of type I rings is decreased and the number and clearness of the type II rings are increased. The number

TABLE XXXVIII

RHYTHMIC BANDS OF FERRO- AND FERRICYANIDES

Jelly	Type of ring	Ferrocyanides of	Ferricyanides of
Gelatin	I	Cu, Zn	Co, Zn, Mn
Gelatin	II	Pb, Ag, Co, Ni, Ba, Fe^{+++}, Sn	Ag, Ni, Fe^{++}
Agar	II	Mn, Ag, Cu, Ni, Zn	
Starch	II	Co, Ni, Ag	

of rings is increased by exposure to light which has a coagulating action on the dispersed salt.

Sols

Gels of the heavy-metal ferrocyanides are easily obtained in the form of stable hydrosols by washing out the excess of electrolytes from the gel or by the addition of a suitable excess of alkali ferrocyanide and dialyzing. By either procedure the sols are negatively charged and are quite stable both because of strong adsorption of the tetravalent potential-determining ions and the low solubility which retards crystal growth.

HEAVY-METAL FERRICYANIDES

The solubility of the heavy-metal ferricyanides is greater than that of the corresponding ferrocyanides; hence the precipitates are more crystalline, less gelatinous, and have a lower adsorption capacity (*cf.* p. 335). The normal salts may be obtained relatively pure by the interaction of alkali ferricyanide and metallic salts especially if the latter are kept in excess. In the titration of salts of silver, copper, cadmium, cobalt, and nickel with potassium ferricyanide by the conductometric method, a break occurs corresponding to complete precipitation of the respective normal salts,[27] whereas with zinc the break occurs 3%

[27] Kolthoff: Z. anal. Chem., **62**, 215 (1923).

below the calculated value for the normal ferricyanide and with manganous salts the titration is erratic probably because of their reducing action. Normal zinc ferricyanide comes down almost pure when precipitated in the hot with alkali ferricyanides.[28]

The double salts with alkali and alkaline-earth ferricyanides are usually definitely crystalline, and the ratio of heavy metal to alkali or alkaline-earth metal is usually a small number.

The salts are too soluble to form stable sols. Copper ferricyanide, probably the most insoluble of the common salts, gives a negative sol which is stable for only a few days.[29]

Special chapters will be devoted to colloidal copper ferro- and ferricyanide and to Prussian blue.

[28] Čuta: Collection Czechoslov. Chem. Commun., **1**, 538 (1929).
[29] Luppo-Cramer: Kolloid-Z., **1**, 353 (1907).

CHAPTER XVII

COLLOIDAL COPPER FERROCYANIDE: THE SOL

The formation, composition, and general properties of precipitated copper ferrocyanide have been considered in the preceding chapter. The hydrous gel like most heavy-metal ferrocyanides is a mordant more especially for basic dyes.[1] The black silver image in an ordinary photographic print may be converted into a red one, consisting in part of copper ferrocyanide, by immersing the print in a copper toning bath which is essentially a sol or solution of copper ferrocyanide in an alkaline salt of citric, tartaric, or oxalic acid, together with other salts.[2] Owing to the mordanting action of the ferrocyanide dye, toned images may be obtained by immersing the copper-toned print in an acid solution of basic dye such as thioflavine, victoria green, methyl green, methylene blue, chrysoidine, or methyl violet.[3]

Formation of Sol

A stable brown sol of copper ferrocyanide results on mixing dilute solutions of copper salt and potassium ferrocyanide with the latter in slight excess.[4] More concentrated sols may be prepared in this way by the use of protecting colloids such as gelatin or by peptizing the freshly formed gel with potassium oxalate,[4] ammonium sulfate,[5] or, preferably, with potassium ferrocyanide.[6] A pure stable, but rather dilute, sol results on rapid, thorough washing of the gel by the aid of the centrifuge, followed by dialysis.[7]

Because of the marked tendency of copper ferrocyanide to carry down alkali ferrocyanides, a sol free from alkali salt is best prepared by peptization with dilute hydroferrocyanic acid of the gel thrown down with copper acetate and the acid.[8] To prepare an easily peptiz-

[1] Clark: Eastman Kodak Co., Abridged Publications, **2**, 130 (1915-16).

[2] Ferguson: Phot. J., 133 (1900).

[3] Crabtree: J. Franklin Inst., **186**, 515 (1918).

[4] Graham: Phil. Trans. **151**, 183 (1861); *cf.* Gurchot: J. Phys. Chem., **30**, 90, (1926).

[5] Pappadà: Kolloid-Z., **9**, 136 (1910); Gazz. chim. ital., **41** II, 470 (1911).

[6] Chakravarti and Dhar: Kolloid-Z., **42**, 124 (1927).

[7] Weiser: J. Phys. Chem., **30**, 1530 (1926).

[8] Weiser and Milligan: J. Phys. Chem., **40**, 1071 (1936).

able gel it is essential to avoid an excess of copper ion both during the initial precipitation and during the repeated centrifugal washing necessary to remove the acetic acid. The secret of the method is to have ferrocyanide ion in very slight excess but not in sufficient amount to prevent the throwing down of the gel with the centrifuge. When properly prepared 10 to 20 g of $Cu_2Fe(CN)_6$ are readily peptized by 1 1 of 0.002 *N* $H_4Fe(CN)_6$ to give a clear red sol in which all the ferrocyanide ion is adsorbed.

Ferrocyanide sols of copper, zinc, and iron in methyl alcohol may be prepared by the interaction of alcoholic solutions of the respective metallic chlorides and hydroferrocyanic acid followed by washing the gels with methyl alcohol until they are peptized, giving clear sols.[9]

General Properties

The negatively charged copper ferrocyanide sols are quite stable, probably because of the high valence of the potential-determining ion. When they are formed in the presence of an appreciable excess of ferrocyanide, their stability toward the chlorides of potassium, barium, and aluminum is decreased but little by boiling; dialysis increases their stability toward the coagulating electrolytes. Chaudhury[10] has studied the change in the mobility of the particles of sols prepared in different ways on dilution and on adding electrolytes both in the presence and in the absence of non-electrolytes. It is difficult to draw any definite conclusions from the observations because of the complexity of the sols employed. The work should be repeated with a sol as nearly monodisperse as it can be made by centrifugal fractionation; and hydroferrocyanic acid should be used in its preparation in order to avoid the presence of the large excess of adsorbed alkali ferrocyanides when these salts are employed.

The relative viscosity of a sol containing 8.5 g $Cu_2Fe(CN)_6$/l was 1.03.[6] This was increased appreciably by adding electrolytes because of agglomeration of the highly hydrous particles into larger aggregates.

Coagulation of Sol by Electrolytes

Coagulation by Single Electrolytes

Duclaux[11] first studied the precipitating action of various cations on a copper ferrocyanide sol. A given volume of sol containing

[9] Weiser and Mack: J. Phys. Chem., **34**, 86 (1930).

[10] J. Indian Chem. Soc., **10**, 431 (1933); Chaudhury and Chatterjee: J. Phys. Chem., **33**, 244 (1929).

[11] J. chim. phys., **5**, 29 (1907).

9.6×10^{-6} gram atom of K^+ required for coagulation the following gram equivalents $\times 10^{-6}$ of the several cations: Ag, 6.6; Cu, 3.4; Al, 5.8; Fe+++, 6.2; UO_2, 15.0; Ba, 48.0; Mg, 98; K, 240. It is claimed that these precipitation values are approximately equivalent, irrespective of the valence, and are of the same order as the potassium ion concentration, provided one considers the first four ions in the above list and disregards the last four. On the basis of these and similar data on hydrous ferric oxide sol, he considers the precipitation process to be a definite stoichiometric chemical action, a double decomposition of the ordinary type. This conclusion is not in accord with the facts, even if one were permitted to disregard the last four ions. The precipitation concentration expressed in equivalents is different for each ion and has no necessary connection with the potassium ion concentration. In accord with the usual rule, the precipitating power of an electrolyte is determined by the adsorbability of the precipitation ion, which is, in general, greater the higher the valence, and by the adsorbability of the ion having the same charge as the sol. This is illustrated by some of the observations of Sen [12] recorded in Table XXXIX. In part *A* are given the precipitation values of salts with cations of varying valence. It will be seen that the elements divide

TABLE XXXIX

PRECIPITATION CONCENTRATION (*X*) OF ELECTROLYTES FOR $Cu_2Fe(CN)_6$ SOL
(Millimols/l)

A Salts with cations of varying valence		*B* Potassium Salts	
Salts	*X*	Salts	*X*
KCl	35 6	KNO_3	28 7
NaCl	92 5	KBr	27 5
$Ba(C_2H_3O_2)_2$	0.445	K_2SO_4	47 5
$BaCl_2$	0 458	K_2HPO_4	47 5
$SrCl_2$	0.538	K_2CrO_4	80 0
$MgSO_4$	0 760	$K_2C_4H_4O_6$	95 0
$Al_2(SO_4)_3$	0 058	$K_2C_2O_4$	170 0
$Ce(NO_3)_3$	0.034	$K_3Fe(CN)_6$	205 0
$Th(NO_3)_4$	0.038	$K_4Fe(CN)_6$	260 0

[12] J. Phys. Chem., **29**, 517 (1925).

themselves into three well-defined groups depending on the valence.[13] In part *B* are given the precipitation values of potassium salts arranged in decreasing order of precipitating power, which is the order of increasing adsorption of the anions, on the assumption that the most strongly adsorbed anion has the most pronounced stabilizing action. The phenomenon of "acclimatization" (p. 197) was observed with chlorides of the alkali metals.[14]

Frankert and Wilkinson[15] determined the acidity or alkalinity developed on shaking solutions of potassium salts with powdered copper ferrocyanide. The hydrogen ion concentration varies from slightly acid with the weakly adsorbed chloride to highly alkaline with the strongly adsorbed ferrocyanide. The order of adsorption of anions based on the acidity developed is: $Fe(CN)_6^{----} > HPO_4 > OH > Fe(CN)_6^{---} > SO_4 > Cl > NO_3$. It will be noted that the order is similar to the one deduced from precipitation data for ions common to both series. It is probable that the series would be more nearly alike for the two sets of experiments if the same sample of copper ferrocyanide were employed.

At this point it may be mentioned that uranyl ferrocyanide sol is similar in appearance and in general properties to copper ferrocyanide sol.[16] The molar precipitating power of cations for the sol is: $Th > Al > UO_2 > Ag > Ba[Cl] > Ba[OH] > H > NH_4 > Na$.[17] With all common electrolytes the precipitation concentration decreases with dilution of sol (*cf.* p. 193). Dilution affects the stability by disturbing the adsorption equilibria of potassium and ferrocyanide ions. When the ferrocyanide content of the sol is kept constant the precipitation concentration varies but little with the content of $UO_2Fe(CN)_6$.

Mechanism of the Coagulation Process

Titration of Sols.[8] Electrolytes were added stepwise to sols prepared by peptization of copper ferrocyanide gel with hydroferrocyanic acid, and the change in concentration of the counter hydrogen ions was followed with the glass electrode. This process is called titration. The method was as follows: 20-cc portions of sol were mixed with a definite quantity of electrolyte diluted to 5 cc and the mixtures allowed

[13] *Cf.* Pappadà: Gazz. chim ital, **41** II, 470 (1911).

[14] Boutaric and Berthier: Bull. soc. chim., (5) **3**, 696 (1936).

[15] J. Phys. Chem., **28**, 651 (1924).

[16] Ghosh and Dhar: J. Phys. Chem., **31**, 187, 649 (1927).

[17] Chatterjee: Kolloid-Z., **52**, 214 (1930); J. Indian Chem. Soc., **12**, 671 (1935).

to stand 4 hours before determining the hydrogen ion concentration. A typical series of experiments with barium chloride as precipitating electrolyte is given in Table XL. In the last column is recorded the adsorption of barium ion at and above the precipitation value.

TABLE XL

TITRATION OF $Cu_2Fe(CN)_6$ SOL WITH $BaCl_2$

0 02 *N* $BaCl_2$ added to 20 cc of sol. Total volume 25 cc	$[H^+] \times 10^3$ in solution	$[H^+] \times 10^3$ displaced	$[Ba^{++}] \times 10^3$ added	$[Ba^{++}] \times 10^3$ adsorbed
0 0	1 29	0 0	0 0	
0 5	1 50	0 21	0 4	
1 0	1 68	0 39	0 8	
1 5	2 03	0 74	1 2	
2 0	2 10	0 81	1 6	
2 5	2 19	0 90	2 0	
3 0	2 19	0 90	2 4	2 22
4 0	2 19	0 90	3 2	
5 0	2 19	0 90	4 0	2 84

For comparing the action of different electrolytes a sol was titrated with the chlorides of barium, strontium, and potassium, and the adsorption of barium and strontium was determined at and above their respective precipitation values. The results are summarized in Fig. 47. The precipitation concentration is indicated by an arrow.

The behavior of the sol toward electrolytes is so much like that of sulfur sol [18] and the hydrous oxide sols (Vol. II, pp. 73, 114, 142) that it can be explained by a similar mechanism. The potential-determining ions are the common ferrocyanide ions, and the counter ions are hydrogen ions. In this respect it is similar to Verwey and Kruyt's silver iodide sol (p. 115) in which the potential-determining ions are the common iodide and the counter ions are hydrogen. On account of the small ionization constant of the fourth hydrogen ion in hydroferrocyanic acid, it is probable that, even in the dilute solutions employed, the anion is chiefly $HFe(CN)_6^{---}$ (represented by R^{---} in Fig. 47) rather than $Fe(CN)_6^{----}$. In any event, the negative ions may be assumed to form the inner portion of a double layer surrounding the hydrous particles of cupric ferrocyanide, as represented diagram-

[18] Weiser and Gray: J. Phys. Chem., **39**, 1163 (1935).

matically in Fig. 48*A*. The counter ions are hydrogen ions which form the diffuse outer portion of the double layer. Some of the hydrogen ions are held so strongly (adsorbed) by the attractive force of the inner layer that they are not detected by a hydrogen electrode, whereas others, because of a relatively higher kinetic energy, exert sufficient osmotic repulsive force against the attraction of the adsorbed ferrocyanide ions that they are a part of the intermicellar solution and thus influence the hydrogen electrode. These are represented in the dia-

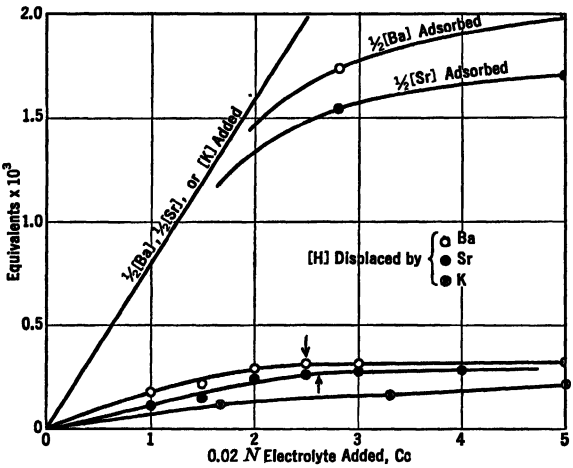


FIG 47.—Adsorption of precipitating cations and the displacement of hydrogen in the titration of copper ferrocyanide sol with the chlorides of barium, strontium, and potassium.

gram beyond the dotted line. On adding an electrolyte such as barium chloride to the sol, the bivalent barium ions are attracted more strongly by the inner layer than the counter hydrogen ions, as shown diagrammatically in Fig. 48*B*, and the thickness of the double layer is reduced. At the same time, some adsorbed hydrogen ions are displaced and are detected in the intermicellar solution. This contraction of the double layer or compression of the outer layer resulting from stronger adsorption of barium ions than hydrogen ions under the prevailing relative concentrations, causes a lowering of the ζ-potential on the particles; when this is reduced sufficiently, coagulation takes place. The displacement of adsorbed hydrogen ions by adsorbed barium ions is far from an equivalent displacement, since most of the adsorbed barium ions correspond to hydrogen ions which are in the intermicellar solu-

tion and so are measurable potentiometrically in the original sol. It is not at all surprising that in certain instances all the adsorbed hydrogen ions are displaced before sufficient barium ions are adsorbed to reduce the ζ-potential to the coagulation point.

Since most of the added barium ions are adsorbed at concentrations slightly *above* the coagulation value, it would follow that most if

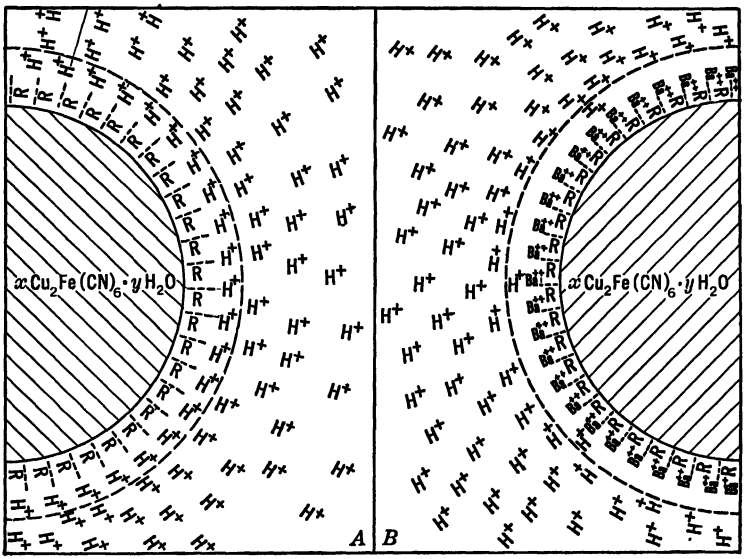


FIG. 48.—Diagrammatic representation of the constitution of a particle in a copper ferrocyanide sol (*A*) before and (*B*) after the addition of barium chloride.

not all the added barium ions are adsorbed *below* the coagulation value. Since the total barium adsorbed above the coagulation value is somewhat greater than the total hydrogen ions in the sol, it follows that, to a certain extent, both barium ions and chloride ions are adsorbed in equivalent amounts from the barium chloride solution. The observed phenomena are almost identical with those using the positive hydrous oxide sols of iron, aluminum, and chromium in which the counter ions are chloride ions and the precipitating electrolyte is potassium sulfate. The behavior of strontium chloride is similar to that of barium chloride, whereas potassium chloride has a lower precipitating power, because potassium ions are less strongly adsorbed and displace hydrogen less strongly than the bivalent ions at the same concentration.

From the above observations it is concluded that the lowering of the ζ-potential of the cupric ferrocyanide particles on the addition of electrolytes is caused by the contraction of the double layer or, if preferred, by a compression of the outer layer resulting from adsorption of the added cations. At all concentrations the cation adsorption is much greater than the hydrogen-ion displacement, since more of the counter ions in the diffuse layer are in the intermicellar solution. The adsorption is for the most part an exchange phenomenon, in which the cations carried down are in exchange with the counter hydrogen ions of the diffuse outer layer. The apparent difference in behavior between the sols investigated by the author and the silver iodide sol studied by Verwey and Kruyt (p. 124) is that in the former the potential reduction results from adsorption of precipitating ions, whereas in the latter adsorption may not be essential for all the potential reduction.

Some observations of Bhatnagar[19] may be of importance for the theory of the electrolyte coagulation process. Various sols were prepared, including copper ferrocyanide, and coagulated by electrolytes with precipitating ions of varying valence. By means of a special elutriating device, it was found that, for sols of one particle size, the ratios of the elutriating velocities for the particles of the coagula obtained by salts with univalent, bivalent, and trivalent precipitating ions are, 1:2:3. A close relationship is thus indicated between size of particles formed by agglomeration and the valence of the precipitating ion. With spherical particles falling in a viscous liquid, the velocity of fall, which corresponds to the elutriating velocity, is proportional to the square of the radius, that is, to the extent of surface of the particles. If Bhatnagar's observations are correct it follows, therefore, that the magnitude of the charge present on the precipitating ion will determine the extent of surface of particles formed by coagulation of sols. Unfortunately, the experimental procedure is open to so many possible sources of error, and the observations are so incomplete, that any deductions based on the recorded data would seem to be premature.

Coagulation by Mixtures of Electrolytes: Ion Antagonism

The phenomena observed in the precipitation of arsenic trisulfide sols by salt pairs were attributed primarily to: (1) ion antagonism between certain cations in the sense that each cuts down the adsorption of the other and (2) the stabilizing effect of anions which opposes the precipitating action of the cations (p. 216). In some systems it is pos-

[19] Bhatnagar, Mathur, and Shrivastava: J. Phys. Chem., **28**, 387 (1924).

sible to eliminate the first effect entirely. Thus Sen,[20] working with copper ferrocyanide sol, observed an increase in precipitation value of potassium chloride and of barium chloride in the presence of potassium ferrocyanide. It is quite obvious with mixtures of potassium chloride and potassium ferrocyanide, that cation antagonism cannot come in, since both precipitating cations are the same. Mukherjee and Ghosh [21] observed a similar behavior with mixtures of sodium benzoate and sodium chloride on arsenic trisulfide sol, and the author confirmed this with potassium ferrocyanide and potassium chloride on the same sol. The determining factor in these systems is the stabilizing action of the relatively strongly adsorbed benzoate and ferrocyanide, respectively.

Consider Graham's ferric oxide sol, which owes its stability to preferential adsorption of hydrogen ion derived from hydrolysis of ferric chloride. The stability of this sol falls off as the hydrogen ion concentration is decreased by dialysis, and if the dialysis is continued long enough all the sol will precipitate; conversely, if hydrochloric acid is added to a highly purified sol, the stability toward all electrolytes will increase. Similar stabilization would be expected on adding ferric chloride, aluminum chloride, or lanthanum nitrate, as Freundlich and Wosnessenski [22] have shown. With the relatively insoluble Péan de St. Gilles sol, a maximum in the stability is reached on adding hydrochloric acid, and at a suitable concentration coagulation takes place.[23] Similarly, the stability of copper ferrocyanide sol falls off with decreasing concentration of the stabilizing ferrocyanide ion. On adding potassium ferrocyanide to a highly purified sol, the stability towards all electrolytes should increase to a maximum and then fall off as the coagulating action of potassium ion begins to predominate. This is exactly what Sen observed with two electrolytes of widely varying precipitating power. The precipitation value of both potassium chloride and barium chloride is increased to a maximum that lies above the value for either electrolyte alone.[24]

The observations of Sen have been confirmed and extended with a highly purified copper ferrocyanide sol.[25] The results with mixtures

[20] J. Phys. Chem., **29**, 354 (1925); J. Indian Chem. Soc., **3**, 81 (1926).

[21] J. Indian Chem. Soc., **1**, 213 (1924).

[22] Kolloid-Z., **33**, 222 (1923).

[23] Weiser: J. Phys. Chem., **25**, 665 (1921).

[24] Sen: J. Phys. Chem., **29**, 517, 539 (1925); Sen and Mehrotra: Z. anorg. Chem, **142**, 345 (1925).

[25] Weiser: J. Phys. Chem., **30**, 1531 (1926); *cf.* Chatterjee: J. Indian Chem. Soc., **12**, 671 (1935).

of potassium ferrocyanide and both potassium chloride and barium chloride are shown graphically in Fig. 49. It will be seen that the addition of potassium ferrocyanide causes the precipitation value of potassium chloride to mount sharply to a value more than six times that of pure chloride. This indicates that the purity of the original sol with respect to ferrocyanide ion is quite high. After the maximum is reached, the curve bends sharply and then follows an almost linear course, as Sen also observed. This means that, if one takes an impure copper ferrocyanide sol, the precipitation values of mixtures of potassium ferrocyanide and chloride will be approximately additive on ac-

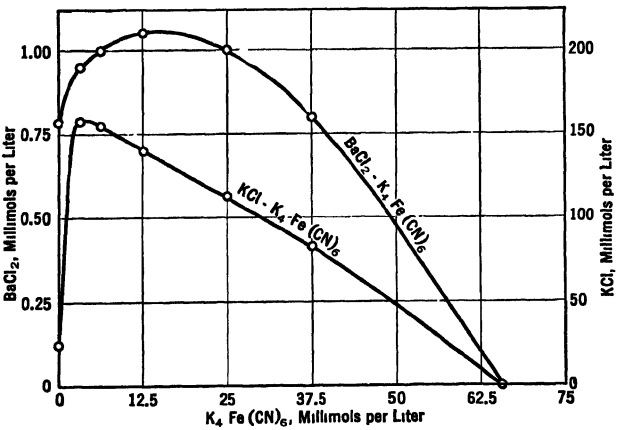


FIG. 49.—Precipitation of copper ferrocyanide sol with mixtures of electrolytes.

count of the absence of cation antagonism. A similar type of curve should result with mixtures of barium ferrocyanide and barium chloride. This was found to be true so far as the linear part of the curve is concerned; but the sharp maximum could not be detected with certainty since the precipitation concentrations of the chloride and ferrocyanide of barium were so close together.

Turning to the potassium ferrocyanide-barium chloride curve, contrary to Sen's observations, one is impressed with the very great similarity to the curves obtained with alkali-alkaline earth salt pairs on arsenic trisulfide sol (p. 220). Since in the latter system both cation antagonism and the stabilizing action of the anion play a rôle, it is possible that the difference between the potassium ferrocyanide-barium chloride curve, and the potassium ferrocyanide-potassium

chloride curve with copper ferrocyanide sol, is caused by the absence of cation antagonism in the first instance and its presence in the second.

It should be emphasized, however, that the initial increase in precipitation value of barium chloride in the presence of potassium ferrocyanide results primarily from the effect of ferrocyanide ion. Thus, the precipitation values of mixtures of potassium chloride and barium chloride fall slightly below the additive value at the lower concentrations of potassium chloride, but at higher concentrations of potassium chloride the values are slightly greater than additive. The same is true for mixtures of potassium chloride and cupric chloride and of potassium chloride and cupric sulfate.[26] For arsenic trisulfide sol the antagonism between potassium and barium ferrocyanide is greater than between the corresponding chlorides; and a similar condition doubtless exists with copper ferrocyanide sols.

Coagulating Action of Alcohols

Copper ferrocyanide sol is precipitated by methyl alcohol in rather high concentration. Gurchot[27] offered two possible explanations of this phenomenon: first, that the coagulation is brought about by a decrease in surface tension; and, second, that the negative charge on the particles is reduced below the critical value by the selective adsorption of alcohol. The second explanation is regarded as the more probable since surface-tension decrease would tend to cause peptization rather than agglomeration. Gurchot implies that the reduction in the negative charge of the ferrocyanide particles is caused by selective adsorption of the positive radical of the alcohol; but, because of the slight polarity of the alcohol molecules, it seems likely that this effect will be negligible. A more probable explanation is that alcohol decreases the adsorption of the stabilizing ferrocyanide ion, either by displacing the latter or by cutting down the ionization of the salt in the intermicellar liquid (p. 200). In accord with this, Sen[28] showed that the purer the sol the greater is its stability toward alcohols. The coagulating power of a series of alcohols is in the order: methyl < ethyl < propyl < butyl.

[26] *Cf., however,* Gurchot. J. Phys. Chem., **30**, 98 (1926).
[27] J. Phys. Chem, **30**, 99 (1926).
[28] J. Indian Chem. Soc., **2**, 289 (1925).

CHAPTER XVIII

COLLOIDAL COPPER FERROCYANIDE AND FERRICYANIDE: THE MEMBRANES

Copper ferrocyanide and ferricyanide furnish such good examples of semipermeable membranes that their behavior in this respect will receive special consideration.

Semipermeable Membranes

Definition

A membrane is said to be semipermeable when it permits one constituent of a solution—usually water—to pass through and does not allow diffusion of the other constituents or one or more of the other constituents. The plasma membranes of cells are natural membranes of this kind. Traube[1] was the first to recognize a similar semipermeability in certain gelatinous precipitates, the so-called precipitation membranes of which copper ferrocyanide is the most familiar example. Such a membrane is obtained by holding a solution of copper sulfate in a glass tube which is subsequently immersed in a solution of potassium ferrocyanide. The film of copper ferrocyanide formed at the junction of the two solutions will allow water to pass through but not dissolved substances such as sugar and certain salts.

If a solution is covered with a layer of the pure solvent, diffusion of the dissolved substances takes place until the concentration throughout the system is the same. The force driving the dissolved substance from the more concentrated to the less concentrated solution until equilibrium is attained is termed osmotic pressure. The existence of this force may be demonstrated by placing a solution in a vessel with semipermeable walls closed except for a capillary tube, and immersing the vessel in pure solvent. Since the septum is, by definition, permeable to the solvent and impermeable to the solute, and since equilibrium will be attained only when the concentrations on both sides are equal, it follows that the solvent must pass through the membrane and dilute

[1] Arch. Anat. Physiol., 86 (1867).

the more concentrated solution. This manifests itself by a rise of liquid in the capillary tube. An unsupported membrane of copper ferrocyanide ruptures so easily that it is not suitable even for qualitative observation of osmotic pressure. To get around this difficulty, Pfeffer [2] deposited the ferrocyanide on the inside of a porous cup by allowing the ions to diffuse into the supporting medium from opposite sides. A more satisfactory method devised by Morse [3] consists in driving the ions into the walls by means of an electric current. Membranes supported in this way have withstood pressures as high as 130 atmospheres and have proved to be nearly ideal as regards semipermeability.

Theories of Semipermeability

Atomic Sieve or Ultrafilter Theory. To account for the action of semipermeable membranes, Traube conceived of them as atomic or molecular sieves through which progressively larger molecules diffused with increasing difficulty. Thus a copper ferrocyanide membrane was believed to be an ultrafilter which contains pores large enough for the small molecules of water to get through but too small to allow the larger sugar molecules to pass. This view was shown to be inadequate by the observations of Tammann,[4] Walden,[5] I. Traube,[6] Barlow,[7] and others [8] who made comparative tests on a number of semipermeable membranes with various diffusing substances. If the action is that of a sieve or ultrafilter, it should be possible to arrange the membranes in a series in the order of their permeability. On the contrary, it was found that a membrane quite impermeable to most substances may be more permeable to some than a membrane which, in general, possesses high permeability. Moreover, the impermeability of a membrane such as rubber to water and its permeability to the much larger molecules of benzene and pyridine cannot be accounted for on the sieve theory. Finally the most recent evidence indicates that a membrane such as copper ferrocyanide is not a static system but a dynamic one

[2] "Osmotische Untersuchungen," Leipzig (1877).

[3] Morse and his collaborators: Am. Chem. J., **26**, 80 (1901); **28**, 1 (1902); **29**, 173 (1903); **34**, 1 (1905); **36**, 1, 39 (1906); **37**, 324, 425, 558; **38**, 175 (1907); **39**, 667; **40**, 1, 194, 266, 325 (1908); **41**, 1, 92, 257 (1909); Berkeley and Hartley: Proc. Roy. Soc. (London), **73A**, 436 (1904); Phil. Trans., **206A**, 481 (1906).

[4] Z. physik. Chem., **10**, 255 (1892).

[5] Z. physik. Chem., **10**, 699 (1892).

[6] Phil. Mag., (6) **8**, 704 (1904).

[7] Phil. Mag., (6) **10**, 1 (1905); Findlay and Short: J. Chem. Soc., **87**, 819 (1905).

[8] Kahlenberg: J. Phys. Chem., **10**, 169 (1906).

capable of undergoing reversible permeability under suitable conditions (p. 338).

The Solution Theory. This theory of the action of the semipermeable membrane postulates that a membrane is permeable to such substances as dissolve in it and impermeable to those that do not. This view was anticipated by Liebig [9] as early as 1848 when he said: "The volume changes of two miscible liquids which are separated from each other by a membrane depend upon the unequal wetting or attraction which the membrane exerts on the two liquids." The first experimental work with the object in view of testing their theory was carried out by Lhermite [10] in 1855. In a test tube he placed some water, above this a thin layer of castor oil, and above this a layer of alcohol. In the course of a few days the alcohol had passed through the castor oil to the water, leaving but two layers in the tube. Turpentine was substituted for the oil with the same results. Again, when a layer of chloroform was separated from a layer of ether by a layer of water, the ether passed through the water to the chloroform. As a result of similar observations on eight different combinations of this kind, Lhermite reached the conclusion that substances which pass through membranes first dissolve in them. This mechanism has been supported by the work of numerous investigators.[11] Thus Kahlenberg found that benzene, toluene, and pyridine, which are soluble in rubber, diffuse through rubber, whereas water which is insoluble in rubber does not pass through. Moreover, trichloroacetic acid passes through a rubber membrane when dissolved in benzene but only very slowly when dissolved in water. Kahlenberg assumed not only a solution of the liquids in membranes to which they are permeable but a kind of loose chemical union as well.

Although solution in the membrane may be a necessary and sufficient criterion for semipermeability in certain systems, Bigelow [12] and Bartell [13] demonstrated conclusively that osmotic effects can be ob-

[9] "Ursachen der Saftebewegung," Braunschweig (1848); Ann., **121**, 78 (1862).

[10] Ann. chim. phys., (3) **43**, 420 (1855).

[11] Graham: Phil. Trans., **144**, 177 (1854); **151**, 183 (1861); Nernst: Z. physik. Chem., **6**, 37 (1890); Tammann: **10**, 255 (1892); Overton: **22**, 189 (1897); Barlow: Phil. Mag., (6) **10**, 1 (1905); Kahlenberg: J. Phys. Chem., **10**, 169 (1906).

[12] J. Am. Chem. Soc., **29**, 1576, 1675 (1907); **31**, 1194 (1909); Bigelow and Robinson: J. Phys. Chem., **22**, 99, 153 (1918).

[13] J. Phys. Chem., **15**, 659 (1911); **16**, 318 (1912); J. Am. Chem Soc., **36**, 646 (1914); **38**, 1029, 1036 (1916).

tained with inert materials where neither solution nor chemical reaction can take place. Thus porous cups served as semipermeable membranes when the pores were sufficiently fine or when they were clogged to a certain extent with such substances as barium sulfate, lead chromate, or lead sulfate. Moreover, finely divided materials such as silica, carbon, and metallic copper, silver, and gold acted as semipermeable membranes when compressed into discs containing very fine pores. The limits of the pore diameters between which osmosis can take place are not definitely known, but they undoubtedly vary from substance to substance. Bartell found the upper limit to be around 0.9 μ with unglazed porcelain clogged with various materials. This is, of course, much too large to represent the dimensions of molecular interstices which Traube believed to be essential for semipermeability in membranes.

The Adsorption Theory. The osmotic phenomena observed with a distinctly porous, non-soluble membrane, such as a clogged porous plate, are doubtless the result of negative adsorption as suggested by Mathieu [14] and Nathansohn [15] and emphasized by Tinker [16] and Bancroft.[17] If a solid adsorbent takes up relatively more of a solvent than of the dissolved substance, we have negative adsorption and the solution becomes more concentrated. Mathieu observed this phenomenon with a number of solutions using porous plates, membranes, or capillary tubes as adsorbents. With normal solutions, the concentration in certain capillary tubes was found to be as low as one-tenth normal. The difference in concentration increases with decreasing radius of the capillary tubes, and Mathieu concludes that with sufficiently fine capillaries water alone would be adsorbed. The importance of this for the theory of semipermeable membranes was recognized especially by Bancroft and by Tinker who gave experimental support to the theory by his work with copper ferrocyanide and sugar solutions.

Sufficiently strong and irreversible positive adsorption by a membrane may render it semipermeable under special conditions (p. 332).

The Copper Ferrocyanide Membrane and Sugar Solution

Since a gelatinous precipitate consists of myriads of particles enmeshed in a network which entrains liquid (Vol. II, p. 9), one might expect the copper ferrocyanide membrane to be porous in the sense

[14] Ann. Physik, (4) **9**, 340 (1902).
[15] Jahrb. wiss. Botan., **40**, 431 (1904).
[16] Proc. Roy. Soc. (London), **92A**, 357 (1916); **93A**, 268 (1917).
[17] J. Phys. Chem., **21**, 441 (1917).

that a very fine porous plate is porous and to be semipermeable because of strong negative adsorption. Tinker[16] examined these artificial membranes microscopically and arrived at the conclusion that they are granular in character[18] with particles having diameters between 100 and 1000 mμ. It is probable that the primary particles are much smaller than this and that what he was measuring was the diameter of secondary particles from partial agglomeration. Indeed, the electron diffraction pattern of the membrane obtained by Fordham and Tyson (p. 308) indicates that the crystal size is not larger than 100–150 Å. In any event, the important thing is that, independently of Mathieu, Nathansohn, and Bancroft, he concluded that negative adsorption in such a porous system is the primary cause of the semipermeability. In support of this view, he demonstrated that cane sugar which ordinarily does not diffuse through a copper ferrocyanide membrane is adsorbed negatively by the salt. Ten-gram samples of finely divided copper ferrocyanide were shaken with sugar solutions of various strengths and the change in concentration determined polarimetrically. From this, the amount of water adsorbed was calculated. The results with four samples dried in different ways and to different degrees are given in Table XLI and shown graphically in Fig. 50. Correction was

TABLE XLI

ADSORPTION OF WATER FROM CANE SUGAR SOLUTIONS BY $Cu_2Fe(CN)_6$

Strength %	Water adsorbed by 100 g of dry $Cu_2Fe(CN)_6$			
	1 Dried completely	2 Dried over H_2SO_4 10 g = 0 689 g H_2O	3 Dried in air at 80° for 3 hours 10 g = 1.38 g H_2O	4 Not dried 10 g = 3 14 g H_2O
5	. . .	.	27 0	
10	18 2	23 9	22 7	24.5
20	15.0		22.5	20.1
40	13 4	18 0	22 2	20 0
60	13 2	14 7	20.8	14.0

made for any water present in the adsorbent before immersing in the solution. It will be seen that sample 3, which had been dried in air,

[18] *Cf., also,* Gurchot: J. Phys. Chem., **30**, 99 (1926).

adsorbs the most water, and sample 1, which was completely dehydrated in a hot oven, adsorbs the least. Complete dehydration is evidently accompanied by partial coalescence with consequent decrease in specific surface.

Tinker believes that the completely dried ferrocyanide first hydrates to $Cu_2Fe(CN)_6 \cdot 3H_2O$ which continues to adsorb water. Since the amount of water in the compound appears to be determined entirely by the conditions of drying, it is probable that no definite hydrate exists (p. 305). So far as the theory of the semipermeable

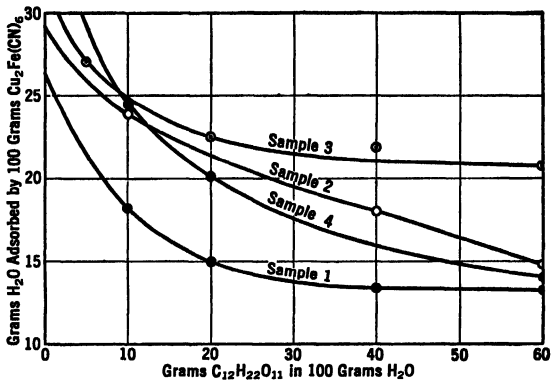


FIG. 50.—Adsorption of water from sugar solutions by copper ferrocyanide gel.

membrane is concerned, it is of course immaterial whether the salt forms a hydrate under any conditions.

Hartung [19] objects to Tinker's conclusion that the impermeability of copper ferrocyanide to sugar results from negative adsorption, on three counts: First, the adsorbent used by Tinker was thoroughly dried copper ferrocyanide powder and not the hydrous gel which constitutes the osmotic membrane. Second, Tinker showed merely that water was adsorbed by the powdered salt more strongly than sugar; but he did not show that sugar was not adsorbed at all. Finally Hartung himself found that potassium sulfate is adsorbed by copper ferrocyanide more strongly than potassium chloride and the sulfate passes the membrane less readily than the chloride. All these objections will be answered in subsequent sections.

[19] Trans. Faraday Soc, **15** (3), 160 (1920).

The Copper Ferrocyanide Membrane and Ferrocyanide Solutions

Although the impermeability to sugar of a copper ferrocyanide membrane may be accounted for by the observed negative adsorption, it is not immediately obvious why the membrane should be impermeable to potassium ferrocyanide. That ferrocyanides do not pass the membrane was pointed out by Tammann, Walden, and Donnan[20] and confirmed by Weiser.[21] Parchment membranes impregnated with copper ferrocyanide do not allow the diffusion of dilute solutions up to *N* $K_4Fe(CN)_6$ into isotonic sugar solutions, and pure water is forced through a membrane when a 0.1 *N* $K_4Fe(CN)_6$ solution is put under pressure in an ultrafiltration apparatus. The greater tendency of the membrane to allow relatively high concentrations to pass probably results from partial coagulation of the colloidal film thereby opening up cracks at weak points in an imperfectly formed septum.

An explanation of the above-mentioned behavior assumes with Collander[22] that the copper ferrocyanide membrane is an ultrafilter or sieve which screens out the relatively large ferrocyanide ion. The objection to this view is that the membrane is permeable to much larger ions and molecules such as phosphomolybdate, so that the screening action is not that of simple ultrafiltration. A second hypothesis is that ferrocyanides like sugar are negatively adsorbed by copper ferrocyanide. This view is contrary to the well-known strong positive adsorption of ferrocyanide ion by the gels. Finally it is assumed that a gelatinous membrane is impermeable to its own ions. This lacks experimental support since the membrane is permeable to copper ion which is much less strongly adsorbed than ferrocyanide.

Referring to Fig. 45 it will be seen that ferrocyanides are adsorbed by copper ferrocyanide in the order: $K_4Fe(CN)_6 > Na_4Fe(CN)_6 > H_4Fe(CN)_6$. The differences would be less marked if it were demonstrated that double salts are formed with the alkali salts (p. 308). But, in every instance, the adsorption is so strong that within a certain range the adsorption is practically irreversible. Therein would seem to lie the explanation of the impermeability of the membrane to ferrocyanide. The adsorption is so strong that the fixed walls of the pores hold chains of oriented molecules extending from a monomolecular film on the surface throughout the pore solution. The practically irreversibly adsorbed ferrocyanide is sufficient to saturate the pore water

[20] Donnan and Allmand: J. Chem. Soc, **105**, 1941 (1914); Donnan and Garner· **115**, 1313 (1919).

[21] J. Phys. Chem., **34**, 335 (1930).

[22] Kolloid-Beihefte, **19**, 72 (1924).

so that no more can enter from the side of the membrane in contact with the solution; and, since the adsorption necessary to saturate the pore solution is not reversible, no ferrocyanide will pass into water or sugar solution on the opposite side. Another way of stating the condition is that ferrocyanide ion is adsorbed so strongly and irreversibly that the actual solution in the pores is practically pure water.

Copper chloride and potassium sulfate are likewise positively adsorbed by copper ferrocyanide (Fig. 45), but the membrane is permeable to them since the relatively weak adsorption is almost completely reversible throughout the entire concentration range. Between one extreme, that of potassium ferryocyanide which will not pass the membrane owing to strong adsorption that is almost irreversible within a certain range, and the other extreme, that of copper chloride which passes the membrane because of relatively weak adsorption that is completely reversible, there are an indefinite number of gradations in the degree of permeability with salts as a result of positive adsorption.

The Copper Ferricyanide Membrane and Sugar Solution [23]

Since a copper ferricyanide membrane is impermeable to cane sugar, it would follow from analogy with the corresponding ferrocyanide that sugar would be negatively adsorbed by the salt from aqueous solution. To test this, copper ferricyanide was precipitated from sugar solution and the change in concentration of the sugar was determined before and after the precipitation. The procedure was as follows: The calculated amount of $CuCl_2 \cdot 2H_2O$ to give 5 g of $Cu_3[Fe(CN)_6]_2$ was dissolved in 50 cc of water in one container of a mixing apparatus,[24] and an equivalent amount of $K_3Fe(CN)_6$ together with a definite weight of sugar was dissolved in 100 cc of water in a second container. After thorough mixing, followed by centrifuging, the concentration of sugar in the supernatant solution was determined in a Reichert Soleil-Ventzke saccharimeter. For comparison, a determination was made of the concentration of a sugar solution containing the same weight of sugar in the same volume of water as above, together with KCl equivalent to 5 g of $Cu_3[Fe(CN)_6]_2$. The results of two experiments with different concentrations of sugar are given in Table XLII. The saccharimeter reading in Ventzke degrees is an average of 20 readings made under carefully controlled conditions. It will be seen that the concentration of sugar is greater

[23] Weiser: J. Phys. Chem., **34**, 1826 (1930).
[24] Weiser: J. Phys. Chem., **34**, 340 (1930).

TABLE XLII

ADSORPTION OF H_2O FROM CANE SUGAR BY $Cu_3[Fe(CN)_6]_2$

Substances mixed in grams					$Cu_3[Fe(CN)_6]_2$ precipitating g	Saccharimeter reading degrees Ventzke	H_2O adsorbed by $Cu_3[Fe(CN)_6]_2$	
$CuCl_2 \cdot 2H_2O$	$K_3Fe(CN)_6$	KCl	Cane sugar	H_2O			g/g	mols/mol
4.1624	5 3570	0 0	8.0	150 0	5 0	19 75		
0.0	0 0	3.6395	8 0	150 88*	0 0	19.30	0 666	22 6
4.1624	5 3570	0 0	13.0	150 0	5.0	31 48		
0.0 ,	0.0	3 6395	13.0	150 88*	0 0	31.05	0 476	16.2

* 4.1624 g $CuCl_2 \cdot 2H_2O$ contains 0 88 g H_2O.

in the solution from which the gel separated; from this increase the adsorption of water given in the last column of the table was calculated.

The results of the above experiments show conclusively that water is adsorbed strongly relatively to sugar by precipitated copper ferricyanide, the extent of the adsorption being greater the more dilute the solution. Since this behavior is similar to that observed by Tinker with dry copper ferrocyanide in sugar solutions, it would seem that Hartung's criticism of the experimental procedure employed by Tinker is not valid.

Although the above results furnish strong evidence in support of the view that the impermeability of copper ferricyanide to sugar is the result of marked negative adsorption, the case would be even stronger if it could be shown that no sugar at all is adsorbed by the precipitated gel. Unfortunately it is difficult to determine the presence of a trace of sugar in the presence of an excess of copper ferricyanide, but the following experiment indicates that little or none is adsorbed: A gram of the ferricyanide gel precipitated in the presence of sugar was washed repeatedly by the aid of the centrifuge until the wash water was free from sugar, using 0.5 *N* KCl solution which prevented peptization of the gel. The suspended gel was digested for a day in dilute hydrochloric acid, a procedure which should invert any cane sugar that might be present. A sample was then subjected to Fehling's test by dissolving the gel in alkaline sodium tartrate solution and heating; the results were negative.

Copper Ferricyanide Membrane and Electrolyte Solutions[23]

Adsorption of Electrolytes. The adsorption of potassium ferricyanide, sulfate, and chloride by copper ferricyanide was determined

by a procedure similar to that used with copper ferrocyanide (p. 306). The results are shown graphically in Fig. 51, in which the adsorption is plotted on a scale twice as large as that in Fig. 45. Potassium ferricyanide is adsorbed by copper ferricyanide gel less strongly than potassium ferrocyanide is by the corresponding ferrocyanide gel. Moreover, the adsorption of ferricyanide is not completely irreversible even at very low concentrations, although the adsorption curve approaches

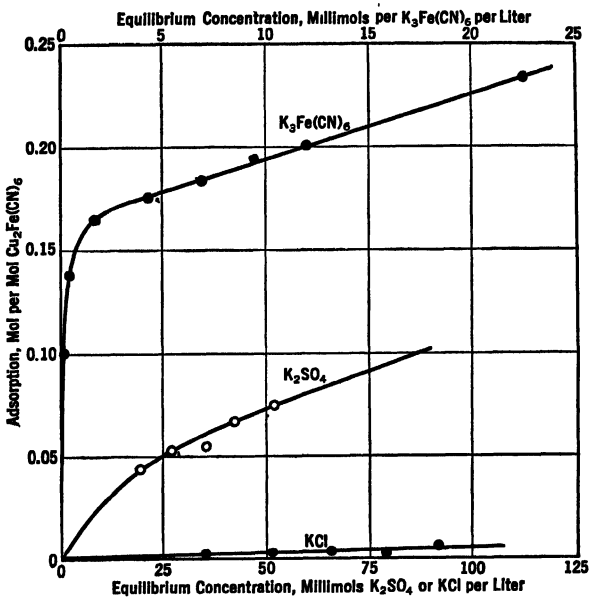


FIG. 51.—Adsorption of potassium salts by copper ferricyanide gel.

quite close to the x-axis. The adsorption of sulfate is considerably greater than that of chloride in accord with Hartung's observations with copper ferrocyanide gel.

Permeability Experiments. Since sufficiently marked positive adsorption of a solute by a membrane may render the membrane impermeable to the solute, one would expect that, other things being equal, the more strongly a solute is adsorbed by a membrane, the more slowly it would diffuse through. It is of course impossible to realize ideal experimental conditions, since the size, extent of hydration, and mobility of the ions and molecules are specific; nevertheless the rate of diffusion of potassium ferricyanide, sulfate, and chloride through a

copper ferricyanide membrane is roughly inversely as their adsorbability by the gel.

Some typical observations are recorded in Table XLIII. Thimbles of parchment were impregnated with copper ferricyanide using special care to obtain a perfect septum. The membranes were suspended to the bottom of a stopper which fitted a 250-cc bottle. After 15 cc of

TABLE XLIII

DIFFUSION OF SALTS THROUGH $Cu_3[Fe(CN)_6]_2$ MEMBRANES

Membrane No	Salt	In cup at start		Outside cup after 24 hours		% diffused through membrane
		cc 0 04 *M*	g	cc 0 04 *M*	g	
1	KCl	15	0 1118	12.75	0 0950	85 0
2	KCl	15	0 1118	12 20	0 0910	81 3
1	K_2SO_4	15	0 1400*	5 74	0 0536*	38 3
2	K_2SO_4	15	0 1400*	5 13	0 0479*	34 2
1	$K_3Fe(CN)_6$	15	0 1975	0 68	0 0089	4 5
2	$K_3Fe(CN)_6$	15	0 1975	0 64	0 0083	4 2

* Calculated in $BaSO_4$ equivalent.

electrolyte was placed in the thimble it was hung in 150 cc of sugar solution isotonic with the electrolyte, and allowed to remain 24 hours. Duplicate experiments were carried out, first with potassium chloride, then with the sulfate, and finally with the ferricyanide, using the same thimbles for each series of observations. The amount of diffusion was determined by analysis of the outside solution. It will be seen that the very strongly adsorbed ferricyanide diffuses quite slowly, the weakly adsorbed chloride quite rapidly, and the sulfate occupies an intermediate position. It appears therefore that the presence of an adsorbed solute in the membrane retards the rate of diffusion of that solute into and through the pores.

Potassium ferricyanide was found to diffuse through a cadmium ferricyanide membrane much more readily than through a copper ferricyanide membrane. There are two reasons for this: first, the adsorption is more readily reversible at low concentrations; and second, the salt is less gelatinous and hence gives a membrane with larger pores.

Summary

The above experimental results support the theory that a membrane will be impermeable to a dissolved solute: (1) provided that it exhibits sufficiently strong negative adsorption that the adsorbed film of pure solvent fills the pores full, or (2) provided that it exhibits sufficiently strong positive adsorption that the pores are filled with a network of oriented chains of adsorbed solute molecules to the point where no more can enter, within the range that the adsorption is practically irreversible.

The adsorption theory of the action of the semipermeable membrane is opposed to the view that the membrane merely acts as a sieve or ultrafilter with pores sufficiently small that dissolved molecules above a certain size are held back while smaller ones can pass through. Nevertheless, pore size is quite as important for the true semipermeable membrane which functions by an adsorption mechanism as it is for the the true ultrafilter which functions as a sieve without the intervention of adsorption phenomena. For example, when a solute fails to pass a membrane because of negative adsorption, the pores must be sufficiently small that the adsorbed film of solvent fills the pores full, otherwise the solute may pass through the center of the pores. In other words, a membrane of a given composition may be impermeable to a solute because of negative adsorption if the pores are small enough and may be permeable to the same solute in spite of negative adsorption if the pores are too large. This does not mean that the porous membrane becomes a molecular sieve or filter when the pores become small enough that the adsorbed film completely fills them. On the contrary, it means that a porous membrane which does not exhibit marked adsorption for a solvent ordinarily acts as an ultrafilter or sieve allowing molecules in solution to pass but holding back particles of colloidal dimensions; but if there is some adsorption of the solvent, and the pores of the membrane are made sufficiently fine, the membrane may become impermeable to certain molecules in solution because of negative adsorption.

In his classical experiments on ultrafiltration Bechhold [25] used collodion which exhibited so little negative adsorption, relatively, that it did not change to a semipermeable membrane at any pore diameter employed. On the other hand, dried collodion membranes with very small pores may not be true molecular sieve membranes or ultrafilters

[25] Z. physik Chem., **60**, 257 (1907).

as is generally assumed.[26] Collander[27] considers such membranes to be molecular sieves through which solutes diffuse at a rate inversely proportional to the molecular size. But he finds that the velocity of diffusion is not determined exclusively by the molecular size and suggests casually that the discrepancies may be caused by solution and adsorption processes in the membrane. Grollman[28] likewise found that the sieve-like action of a collodion membrane is influenced by a layer of adsorbed liquid on the pore walls.

Reversible Permeability of Membranes

A copper ferrocyanide membrane in water is a negatively charged colloidal film analogous to a sol. Since pore size is as important in a true semipermeable membrane as in a true ultrafilter, it follows that the permeability of a copper ferrocyanide membrane to sugar will be increased by the presence of any contiguous solute which causes it to undergo partial agglomeration. This is apparently what happens in certain instances cited by Bancroft and Gurchot.[29] For example, Barlow[30] found that alcohol makes a copper ferrocyanide membrane permeable to sugar. Since sugar is insoluble in alcohol, this permeability cannot be the result of increased solubility of sugar in the membrane. Similarly, Czapek[31] observed the exosmosis of tannin from cells of *Echiveria* which were exposed to the action of various alcohols; the critical concentration for methyl alcohol was about 15%; for ethyl, 10–11%; for propyl, 4–5%; for butyl, 1–2%; and for amyl, 0.5%. Since the above solutions possess a surface tension about 68% that for pure water, Czapek suggested that the surface-tension lowering was responsible for the exosmosis. In view of the fact that tannin is in colloidal solution, it is more likely that the exosmosis was due to partial coagulation of the cell membrane by the alcohols. In support of this view, Gurchot showed that copper ferrocyanide membranes are rendered permeable to sugar by suitable concentrations of the several alcohols.[32] Since a sol of copper ferrocyanide is precipitated by alcohol

[26] *Cf.* Michaelis: Colloid Symposium Monograph, **5**, 135 (1927); J. Gen. Physiol., **8**, 33 (1925); Michaelis and Perlzweig: **10**, 575; Michaelis, Ellsworth, and Weech: 671 (1927); Michaelis and Fujita: Biochem. Z., **161**, 47 (1925).

[27] Soc. Sci. Fennica Commentationes Biol., (6) **2**, 1 (1926).

[28] J. Gen. Physiol., **9**, 813 (1926).

[29] J. Phys. Chem., **28**, 1279 (1924); Gurchot: **30**, 83 (1926).

[30] Phil. Mag., (6) **10**, 1 (1905); **11**, 595 (1906).

[31] Ber. deut. botan. Ges., **28**, 159 (1910).

[32] *Cf., also,* Sen: J. Indian Chem. Soc., **2**, 289 (1925).

(p. 325), it is reasonable to suppose that the dilute alcohol solutions in contact with the membranes cause partial agglomeration, giving pores so large that the film of adsorbed water does not fill them completely and so allows sugar to pass. Salts such as sodium chloride and calcium chloride likewise render the membranes permeable to sugar. The critical concentration was about 2% for sodium chloride and below 1% for calcium chloride which contains the more strongly adsorbed bivalent ion. Below the critical concentration, the salts will dissolve in the adsorbed water layer and will pass through the membrane by osmosis without coagulating it. But when the salt concentration is sufficiently high to neutralize the negative charge on the ferrocyanide below a critical value, partial agglomeration gives pores through which both the salts and sugar can pass by diffusion. When a dilute solution of copper sulfate was placed on one side of a membrane and one of potassium ferrocyanide on the other side, the membrane did not become permeable to sugar in the presence of alcohol or salts, the membrane-forming reagents preventing the formation of effective pores. This observation suggested that a membrane rendered permeable to sugar by alcohols could be made impermeable once more by the addition of a suitable peptizing agent. Gurchot claims to have accomplished this reversal by the use of copper sulfate. It was assumed that copper ion was the peptizing ion from analogy with the behavior of the silver halides; but since copper ferrocyanide is usually negative it is quite as likely that sulfate ion which is fairly strongly adsorbed is the effective one.

Although the permeability of a copper ferrocyanide membrane for sugar will be increased by partial agglomeration and be restored by repeptization, it seems to the author that such a mechanism need not be invoked in all cases to account for change in permeability. The degree of semipermeability in a given membrane is determined by the extent of the negative adsorption and the size of the pores. If the negative adsorption is not sufficiently marked, or if the pores are too large, the pores will not be filled completely with the adsorbed film and so will be more or less permeable. Now it is altogether probable that the extent of the negative adsorption will be influenced by the magnitude and sign of the charge on the colloidal particles and the nature of any adsorbed ions. If this be true, it follows that the presence of electrolytes will influence the amount of the negative adsorption and so will change the permeability altogether apart from any agglomeration or peptization. The important thing, in any case, is that a membrane such as copper ferrocyanide is a dynamic system

which varies in permeability with the nature of the surrounding medium and which is capable of reversible permeability under suitable conditions. Since it is fairly well established that the cell is surrounded by a semipermeable membrane comparable in certain respects to copper ferrocyanide, this concept enables one to account for a number of apparently contradictory facts in connection with the permeability of living cells.

The composition of the cell wall is not known, nor is it known what makes it semipermeable, let alone how the permeability is altered. There can be no doubt, however, that the cell, in pursuing its metabolic functions, does change its permeability in some way. Overton[33] assumes that living cells are surrounded by a lipoid film. This in itself would account for a great many of the permeability phenomena, but such a film would not let water through and it is known that water does get through. Moreover, a great many acid dyes which are insoluble in lipoids penetrate certain cells readily. More striking still is the fact that the cells are normally impermeable to fruit sugar, cane sugar, and other carbohydrates, the amino acids, the acid amides, and many other substances which are foodstuffs for the cells and must get into the cells from the outside. It is this condition which leads Höber[34] to remark: "What the cell can use it shuts out, and what it cannot use it lets in."

The only way to account for these apparently contradictory facts is to assume that the cell may be permeable to a given substance under certain conditions and impermeable under others. Collander[35] contends that protoplasm probably acts as an ultrafilter toward substances which are not soluble in lipoids; but in doing so he has neglected to distinguish clearly between a semipermeable membrane and an ultrafilter and has failed to take into account the important fact that under suitable conditions cells are both permeable and impermeable to the same substance. Moreover, Collander reasons from analogy with the behavior of copper ferrocyanide membranes with the membrane-forming reagents on either side. He thus takes it for granted that cells always have the membrane-forming reagents on either side of them. This assumption is probably erroneous; in any event, it goes well beyond our present knowledge.

[33] Z. physik. Chem., **22**, 189 (1897); Pflugers Arch., **92**, 115, 261 (1902).

[34] "Physikalische Chemie der Zelle und der Gewebe," 5th ed, Part I, 503 (1922).

[35] Kolloid-Beihefte, **19**, 72 (1924); **20**, 273 (1925).

The Theory of Membrane Equilibria

Donnan's theory of membrane equilibria (Vol. 1, p. 315) deals with the equilibria resulting when a membrane separates two electrolytes containing one ion which cannot diffuse through the membrane. Donnan showed that, if one starts with two completely ionized electrolytes, NaCl and NaR, separated by a membrane impermeable to the ion R, equilibrium will be established only when the product of the concentration of sodium and chloride ions has the same value on both sides of the membrane, thus

$$[Na^+]_1 \times [Cl^-]_1 = [Na^+]_2 \times [Cl^-]_2$$

where $[Na^+]_1$ and $[Cl^-]_1$ are the molar concentrations of sodium and chloride ions on one side of the membrane and $[Na^+]_2$ and $[Cl^-]_2$ are corresponding concentrations on the opposite side of the membrane. When equilibrium is reached, if the concentrations in one solution are xNa and xCl, and in the other $(y + z)$Na, yCl, and zNaR, the equation of products becomes

$$x_2 = y(y + z)$$

It is obvious that x must be greater than y so long as z has a finite value; hence the concentration of chloride ion in the first solution must be greater than in the second, whereas the concentration of sodium ion must be greater in the second than in the first. This gives rise to a potential difference E across the membrane which is represented by the equation

$$E = \frac{RT}{F} \log \frac{x}{y}$$

in which R is the gas constant, T the absolute temperature, and F the faraday.

The accuracy of these deductions has been established by investigations on a number of systems, for example: (1) with solutions of potassium chloride and lithium chloride using a layer of amyl alcohol as a membrane;[36] (2) with solutions of Congo red and sodium chloride using a parchment membrane;[36] and (3) with solutions of potassium and sodium chloride and potassium and sodium ferrocyanide, respectively, using a copper ferrocyanide membrane,[20] especially when

[36] Donnan and Harris: J. Chem. Soc., **99** (1), 1554 (1911).

activities are substituted for concentrations.[37] It is of interest to inquire into the nature of the action of the membrane in each instance. In the first example, the amyl alcohol acts as a non-porous semipermeable membrane in which the lithium chloride dissolves and passes through and the potassium chloride does not. In the second example, the parchment functions as an ultrafilter or dialyzing membrane, the concentration, osmotic, and electrical effects being caused by the inability of the large ionic micelle of the colloidal electrolyte to diffuse through the pores. In the third example, the copper ferrocyanide acts as a semipermeable membrane for ferrocyanide ion according to the mechanism described in this chapter.

[37] Kameyama: Phil. Mag., **50**, 849 (1925).

CHAPTER XIX

PRUSSIAN BLUE AND RELATED PRODUCTS

The most important of the iron cyanogen derivatives are the various blue hydrous substances comprised under the general names Prussian or Berlin blue and Turnbull's blue, discovered by Dippel in Berlin in the first decade of the fifteenth century. The blue products are important pigments, and the ease with which they may be obtained in the sol state has led to their use in the investigation of colloid chemical phenomena.

Prussian Blue Gels

Formation and Composition

The common blue iron cyanogen compounds are obtained: (1) by the interaction of ferric salts and ferrocyanides, (2) by the interaction of ferrous salts and ferricyanides, (3) by the oxidation of ferrous ferrocyanide, and (4) by the reduction of ferric ferricyanide. The freshman is usually told that the product of the first reaction is ferric ferrocyanide, $Fe_4{+}{+}{+}[Fe(CN)_6]_3{-}{-}{-}{-}$ or Prussian blue, and the product of the second reaction is ferrous ferricyanide, $Fe_3{+}{+}[Fe(CN)_6]_2{-}{-}{-}$ or Turnbull's blue. It is known, however, that on mixing either a ferric salt and a ferrocyanide, or a ferrous salt and a ferricyanide, the following equilibrium is set up before precipitation begins:

$$Fe^{+++} + Fe(CN)_6^{----} \rightleftarrows Fe^{++} + Fe(CN)_6^{---}$$

This equilibrium is disturbed by the formation of a precipitate, the composition of which is determined by the solubility relations which exist. As a result of extended investigations, Hofmann[1] concluded that all the blue gels are ferrocyanides, derivatives of hydroferrocyanic acid in which the hydrogen is either wholly replaced by ferric iron or partly by ferric iron and partly by another metal. Hofmann

[1] Ann., **337**, 1 (1904); **340**, 267; **342**, 364 (1905); **352**, 54 (1906); J. prakt. Chem., (2) **80**, 150 (1909); *cf., also,* Skraup: Ann., **186**, 385 (1877); Vorländer: Ber., **46**, 181 (1913); Bowles and Hirst: J. Oil and Colour Chem. Assoc., **9**, 153 (1926).

believed that, when alkali (X) ferro- or ferricyanides are employed, the resulting hydrous gels were $Fe_4{}^{+++}[Fe(CN)_6]_3{}^{----}$ or $XFe^{+++}[Fe(CN)_6]^{----}$ or a mixture of the two. Müller[2] confirmed and extended the work of Hofmann by mixing various solutions and determining the course of the reaction by indirect analysis of the precipitates and by electrometric titration. The procedure consisted in mixing definite volumes of Fe^{+++} and $Fe(CN)_6{}^{----}$ or Fe^{++} and $Fe(CN)_6{}^{---}$ of known composition and analyzing the supernatant solution after precipitation to determine the ratio of complex bound iron to iron not present in a complex, and the ratio of Fe^{++} to Fe^{+++}. From such data the composition of the several precipitates was calculated. On adding $K_4Fe(CN)_6$ to $FeCl_3$ in gradually increasing proportions the following compounds appear to form in order: $Fe_4{}^{+++}[Fe(CN)_6]_3{}^{----}$, $KFe^{+++}[Fe(CN)_6]^{----}$, and $K_2Fe^{++}[Fe(CN)_6]^{----}$. When the ratio of $FeCl_3$ to $K_4Fe(CN)_6$ is 4 or more to 3, the product is the normal salt $Fe_4[Fe(CN)_6]_3$, but in other proportions the product is a mixture of this compound with the alleged double salts. Similar observations on adding increasing amounts of $K_3Fe(CN)_6$ to $FeCl_2$ solution indicate the formation of the following substances in order: $KFe_2{}^{++}Fe_5{}^{+++}[Fe(CN)_6]_5{}^{----}$, $KFe^{++}Fe_3{}^{+++}[Fe(CN)_6]_3{}^{----}$, $KFe^{+++}[Fe(CN)_6]^{----}$, and $Fe_4{}^{+++}[Fe(CN)_6]_3{}^{----}$. Intermediate compositions are assumed to be mixtures.

When the ratio of complex cyanide to iron in solution is 1:1 the product can be represented by the formula $KFe[Fe(CN)_6]$ which is formed in accord with the equations:

$$K_4Fe(CN)_6 + FeCl_3 \rightarrow KFe[Fe(CN)_6] + 3KCl$$

$$K_3Fe(CN)_6 + FeCl_2 \rightarrow KFe[Fe(CN)_6] + 2KCl$$

The alleged double salt $KFe[Fe(CN)_6]$ is peptized by water and is called soluble blue. Since the product has essentially the same composition whether one starts with a ferric salt and ferrocyanide, or a ferrous salt and ferricyanide, there would appear to be no distinction between the so-called "soluble" Prussian blue and "soluble" Turnbull's blue. Reihlen and Zimmermann[3] considered the blue products to be

[2] Müller and Stanisch: J. prakt. Chem., (2) **79**, 81; **80**, 153 (1909); **84**, 353 (1911); Müller: **90**, 119 (1914); Müller and Lauterbach: **104**, 241 (1922).

[3] Ann., **451**, 75 (1926); *cf.* Justin-Mueller: Bull. soc. chim., (4) **49**, 1285 (1931).

polynuclear structures rather than salts of hydroferrocyanic acid, but this is denied by Davidson and Welo.[4]

Referring to the above equations, it will be seen that analogous solutions would result if 1 mol KCl is added to the second. Müller and Lauterbach titrated electrometrically: (*a*) $FeCl_3$ with $K_4Fe(CN)_6$; and (*b*) the reverse of (*a*); (*c*) $FeCl_2$ with $K_3Fe(CN)_6$ in

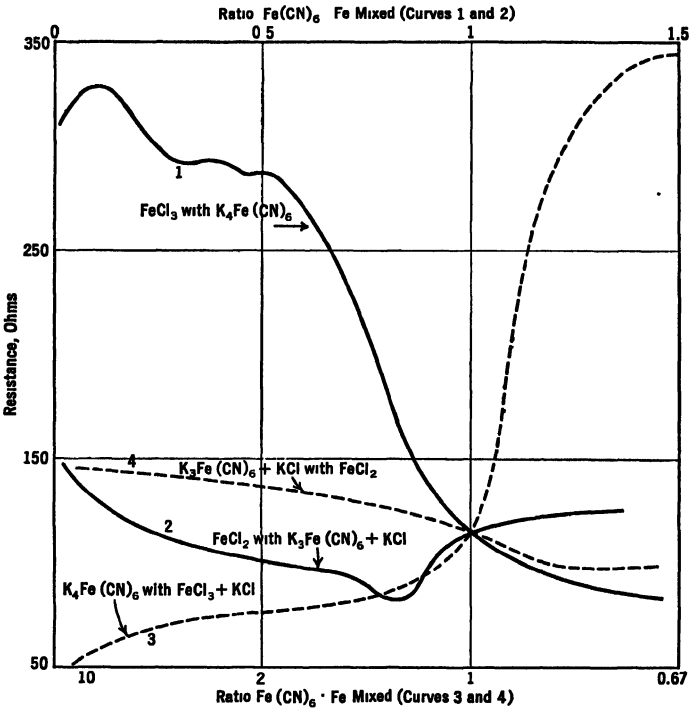


FIG. 52.—Electrometric titration curves for iron salts and complex iron cyanides.

the presence of 1 mol KCl; and (*d*) the reverse of (*c*). The four titration curves shown in Fig. 52 all cut at a single point which indicates (1) that the precipitates corresponding to this point have the same composition for all reactions and (2) that the precipitates formed with other mixtures vary more or less in composition.

Although the work of Hofmann and of Müller has gone a long

[4] J. Phys. Chem., **32**, 1191 (1928).

way toward clearing up the chemistry of the complex iron-cyanogen compounds, there is still considerable doubt as to whether such alleged compounds as $KFe_2{+}{+}Fe_5{+}{+}{+}[Fe(CN)_6]_5{-}{-}{-}{-}$ actually exist. One cannot emphasize too strongly that the analysis of a gel, either by a direct or an indirect method, does not give sufficient data to establish the gel as a definite compound.[5] Electrometric titrations, likewise, cannot give conclusive results when a gel with a strong adsorption capacity is precipitated during the process. Müller believes that the mixtures of varying composition are solid solutions of normal salts and the alleged double salts. It is useless to speculate on this point until we know whether the alleged double salts are definite compounds or adsorption complexes of $Fe_4[Fe(CN)_6]_3$ and alkali ferrocyanide. It is altogether probable that these questions could be settled by systematic x-ray and electron diffraction studies. In this connection Levi[6] claims that the x-radiograms of the so-called Prussian blue and Turnbull's blue are the same. A definite crystalline compound having the formula $KFe{+}{+}{+}[Fe(CN)_6]{-}{-}{-}{-}\cdot H_2O$ is obtained by diluting a hydrochloric acid solution of Prussian blue.[7] It is unlike the gel in that it is not peptized either by water or oxalic acid and has a violet or purple color from which it derives its name, Williamson's violet.[8] X-ray analysis might disclose whether the larger crystals of Williamson's violet are the same in composition and structure as the much smaller crystals of Prussian blue.

Tarugi[9] claims from analysis of numerous blues that a percentage of oxygen is present in all of them that cannot be attributed to analytical errors. The result was confirmed in various ways with highly accurate analytical procedures and with reciprocal control. This is not at all surprising when the blue is made by the interaction of ferrocyanide and ferric chloride, since the iron salt is partly hydrolyzed giving colloidal hydrous ferric oxide which will be carried down by the gel. Indeed Vorländer[10] showed that this hydrolysis of ferric salts causes the reaction with ferrocyanide to proceed at a rate sufficiently slow to measure. In this connection, mention should be made

[5] *Cf* Bhattacharya and Dhar: Z. anorg. Chem., **213**, 240 (1933).

[6] Giorn. chim. ind. applicata, **7**, 410 (1925).

[7] Hofmann, Heine, and Höchtlen: Ann., **337**, 1 (1904).

[8] Williamson: Ann., **57**, 225 (1846); Hofmann, Heine, and Höchtlen· **337**, 1 (1904).

[9] Gazz. chim. ital., **55**, 951 (1925); *cf.* Baudish and Bass: Ber., **55B**, 2698 (1922).

[10] Ber., **46**, 181 (1913); Kolloid-Z., **22**, 103 (1918).

of Reitstötter's [11] observation that the addition of a small amount of ferric salt to the test tube containing the precipitate thrown down from an alumina sol by the required amount of ferrocyanide does not give Prussian blue until after an appreciable interval of time. This is explained by the very strong adsorption of ferrocyanide by alumina which removes the former completely from the field of action. If another strongly adsorbed anion is added to the alumina either before or after coagulation, the ferrocyanide is displaced in part and the time required for the appearance of Prussian blue is diminished appreciably.

"Soluble" and "Insoluble" Blue Products. With $K_4Fe(CN)_6$ in excess and Fe^{+++}, or with $K_3Fe(CN)_6$ in excess and Fe^{++}, a gel results which is readily peptized by water and is called soluble Prussian blue. According to Müller and Lauterbach it is chiefly $KFe^{+++}[Fe^{++}(CN)_6]$ with adsorbed water. With $K_4Fe(CN)_6$ and Fe^{+++} in excess a blue gel is obtained having the composition $Fe_4^{+++}[Fe^{++}(CN)_6]_3^{----}$ which is not easily peptized by water and is therefore called insoluble Prussian blue. A similar product prepared with $K_3Fe(CN)_6$ and Fe^{++} is said to have the formula $Fe^{++}[Fe^{+++}(CN)_6]_2^{---}$ or $KFe^{++}[Fe^{+++}(CN)_6]_3^{---}$ and is called insoluble Turnbull's blue. Insoluble Prussian blue may be distinguished from the corresponding Turnbull's blue with ammonium fluoride which decolorizes the latter but not the former.[12] As we shall see (p. 349), the terms "soluble" and "insoluble" as applied to the blue products are misnomers.

Precipitates in Gels. An experiment in diffusion which involves the formation of Prussian blue is Alexander's so-called "patriotic tube" experiment. A test tube is filled two-thirds full of a slightly alkaline agar sol containing enough phenolphthalein to turn it pink, and a little potassium ferrocyanide. After the agar has set to a solid, a dilute solution of ferric chloride is carefully poured on top. The ferric ion forms with the ferrocyanide a slowly advancing band of blue before which the more rapidly diffusing hydrochloric acid spreads a white band as it discharges the pink color of the indicator. In a few days the tube is about equally banded in red, white, and blue.[13] Creighton [14] obtained rhythmic bands of Prussian blue by passing an electric cur-

[11] Kolloid-Z., **21**, 197 (1917); Freundlich and Reitstötter: **23**, 23 (1918); Vorländer: **22**, 103 (1918).

[12] Szebellédy: Z. anal. Chem., **75**, 165 (1928).

[13] *Cf.* Holmes: "Laboratory Manual of Colloid Chemistry," 11 (1925).

[14] J. Am. Chem. Soc, **36**, 2357 (1914); *cf.* Peskov and Saprometov: Kolloid-Z., **69**, 181 (1934).

rent through a dilute solution of potassium ferrocyanide and sodium chloride in an agar jelly contained in a tube 70 cm long and 2 cm in diameter.

Applications

Commercial Prussian blue is a very important blue pigment. What is said to be the finest variety, known as Paris blue, is obtained by mixing potassium ferrocyanide and ferrous sulfate, followed by oxidation of the white ferrous ferrocyanide by chlorine.[15] The use of potassium salts is said to be important, the color being less satisfactory when sodium salts are employed. Eibner and Gerstacker[16] claim that blues with a high potassium content possess the technically desirable greenish shade whereas those poor in potassium are dull with a violet tinge. It is not obvious why sodium salts should yield a pigment inferior in color to potassium salts. Since the variation in color is determined largely by the physical character of the precipitate, there is no apparent reason why a proper control of the conditions of precipitation should not yield a satisfactory product with sodium salts. Williams[17] claims that potassium salts may be replaced by ammonium salts with satisfactory results.

In commercial pigments, Prussian blue is diluted with starch, heavy spar, gypsum, zinc white, or burned and ground kaolin. The white constituent is first pulverized and then added to a paste of Prussian blue. The relative degree of subdivision of the white and colored constituents is quite important. If a very fine powder is shaken with a moderately coarse one, the former tends to coat the latter instead of filling the voids between the coarser material. In one experiment, Briggs[18] mixed 0.032 g of Prussian blue with 10 g of dolomite which passed a 40-mesh sieve and did not pass a 100-mesh sieve; and in a second experiment, the same amount of Prussian blue was mixed with 10 g of dolomite all of which would pass a 200-mesh sieve. In the first experiment, the resulting mixture was a deep blue and in the second it was practically white although the percentage compositions were identical.

[15] *Cf.* Thorpe: "Dictionary of Applied Chemistry," **2**, 448 (1921)

[16] J. Soc. Chem. Ind., **31**, 1041 (1912).

[17] "The Chemistry, Manufacture, and Estimation of Cyanogen Compounds," 120 (1915).

[18] J. Phys Chem., **22**, 216 (1918); *cf.* Fink: **21**, 32 (1917).

Prussian Blue Sols

Formation

Prussian blue gel precipitated with a small excess of ferrocyanide is called "soluble" Prussian blue because it is so readily peptized to a clear sol by washing. The gel formed in the presence of a slight excess of iron is not peptized by washing and so is designated "insoluble" Prussian blue. As already pointed out, these terms are misnomers. The "soluble" blue is peptized and not dissolved in water, and the freshly formed "insoluble" blue is carried into the sol state by thorough washing with the aid of the centrifuge, especially if a trace of potassium ferrocyanide is added to the wash water.[19] A sol is formed also by peptization of the gel with oxalic acid,[20] followed by dialysis. Unlike oxalic acid, the neutral oxalates of potassium, sodium, and ammonium dissolve the Prussian blue gel, giving a soluble potassium iron oxalate with a green color.[21] Hence the test for ferric iron by the Prussian blue test loses its reliability in the presence of neutral oxalates. The oxalic acid sol was once employed as an ink but it has now been replaced by the blue aniline colors.

Clear blue sols result directly on mixing potassium ferrocyanide and ferric chloride, provided that the ferrocyanide is present in suitable excess and that the concentration is not too great. Zsigmondy[22] titrated 30 cc of 0.1 *M* $K_4Fe(CN)_6$ with 0.1 *M* $FeCl_3$: with 26 cc of the latter solution the sol was clear blue; with 27 cc, partial precipitation was observed; and with 29 cc, precipitation was complete. A stable sol resulted on mixing 0.2% $K_4Fe(CN)_6$ with 1% less than the amount of 0.5% $FeCl_3$ required for precipitation, followed by dialysis.

The addition of an excess of potassium ferrocyanide to a ferric chloride solution gives a blue-green to light-green sol[19] which is not a definite green double salt or other compound. Instead, it is a mixture of very finely divided Prussian blue with a small amount of adsorbed colloidal hydrous ferric oxide; a similar green sol results on mixing a dilute sol of ferric oxide with Prussian blue. The addition of alcohol, hydrochloric acid, or neutral salts, including an excess of potassium

[19] Bachmann: Z. anorg Chem., **100**, 77 (1917).

[20] Stephen and Nash. Ann. Pharm, **34**, 348 (1840); Karmarsch: J. prakt. Chem, **20**, 175 (1840); Graham: Phil. Trans., **151**, 183 (1861); Reindel: J. prakt Chem., **102**, 38, 255 (1867).

[21] Kohn: Monatsh., **43**, 373 (1923); Kohn and Benczer: **44**, 97 (1923); *cf., however,* Buzágh: Kolloid-Z., **44**, 156 (1928).

[22] "Lehrbuch Kolloidchemie," Leipzig, 5th ed., **2**, 160 (1927).

ferrocyanide, to the green sol throws down the usual deep blue precipitate.

In this connection attention may be called to the brown sol of ferric ferricyanide which is formed by the interaction of aqueous solutions of ferric chloride and potassium ferricyanide.[23] Ultramicroscopic examination shows that the particles increase in size gradually and finally deposit a green substance which is probably a mixture of ferric ferricyanide and Prussian blue. A similar green substance is formed by adding ferric chloride to potassium ferricyanide solution containing a little potassium ferrocyanide. Williams[24] believes the gel to be a double salt of ferric ferricyanide and potassium ferric ferrocyanide which he formulates $Fe_{29}{}^{+++}K_3[Fe^{++}Fe_2{}^{+++}(CN)_{18}]_9 \cdot 210H_2O$. Like so many alleged complex compounds, the gel in question is doubtless nothing more than a mixture which can have any composition you like, depending on how it is made.

General Properties

Prussian blue sols are composed of non-spherical particles[25] which are negatively charged as a rule owing to preferential adsorption of ferrocyanide ion. Bachmann showed, however, that the particles are positively charged in the presence of a suitable small excess of the strongly adsorbed ferric ion. The behavior is thus analogous to that of the silver halides which assume a negative charge in the presence of excess halide ion and a positive charge in the presence of excess silver ion. The positive Prussian blue sol precipitates slowly on standing but is completely repeptized by shaking. The stability of the sol is increased by the presence of small amounts of gelatin.[26]

The size of the colloidal aggregates in a sol falls off with increasing concentration of the peptizing ferricyanide ion. Bechhold[27] found that a Prussian blue sol is held back by an ultrafilter which allows a Bredig platinum sol to go through. The addition of the protecting colloid sodium "lysalbinate" to Prussian blue sol peptizes the latter sufficiently to allow it to pass through a filter that stops it before. Nistler[28] estimated the particle radius of a commercial, soluble Prussian blue to be 114×10^{-8} cm.

[23] Haller: Kolloid-Z., **20**, 76 (1917).

[24] "The Chemistry, Manufacture, and Estimation of Cyanogen Compounds," 142 (1915).

[25] Szegvari: Z. physik. Chem., **112**, 277 (1924).

[26] Lobry de Bruyn: Rec. trav. chim., **19**, 236 (1900).

[27] Z. physik. Chem., **60**, 257 (1907).

[28] Kolloid-Beihefte, **31**, 1 (1930).

The sol is very stable at room temperature but is coagulated by boiling and by visible and ultraviolet light and β-rays but not by α-, γ-, or x-rays.[29] The flocculation time is proportional to the concentration and to the thickness of the layer of sol exposed. The optimum wave length for most rapid coagulation is in the neighborhood of 420 mμ. Immediate and complete coagulation takes place on subjecting the sol to a pressure of 2000 atmospheres.[30]

Gatterer[31] has determined the density, viscosity, electrical conductivity, freezing point, and solvent action for carbon dioxide and acetylene, of sols formed by peptization with varying concentrations of sodium ferrocyanide.

Prussian blue sol is hydrolyzed by boiling, giving a negatively charged sol of hydrous ferric oxide.[32]

Coagulation by Electrolytes

Action of Salts. Prussian blue sols are precipitated readily by electrolytes, especially those with multivalent cations. Pappadà[33] found the order of precipitating power to be: Fe, Al, Cr > Ba, Cd > Sr, Ca > H > Cs > Rb > K > Na > Li. Lachs and Lachman[34] investigated the precipitating power of salts with cations of the same valence. The results are given in Table XLIV. On the basis of these and similar observations on colloidal antimony pentoxide, it was concluded that the adsorption of an ion which determines its precipitating power is closely related to its degree of hydration. According to Fajans,[35] the hydration of an ion may be regarded as the formation around the ion of a polarized water envelope consisting of dipoles, the process being accompanied by a positive heat effect. From this point of view, one would expect the adsorption of the ions to be accompanied by partial dehydration, the extent of which will be determined by the heat of hydration of the ions. Since both the heat of hydration and the amount of hydration decrease in the series from lithium to

[29] Lederer and Hartleb: Kolloid-Z, **62**, 42 (1933); Schoras: Ber., **3**, 11 (1870); Ghosh and Dhar: J. Phys. Chem, **30**, 1564 (1926); *cf*, *however*, Roy and Dhar: **34**, 122 (1930).

[30] Wilson and Poulter: Proc Iowa Acad. Sci, **36**, 295 (1929).

[31] J. Chem. Soc., 299 (1926); *cf., also,* Chakravarti and Dhar: Kolloid-Z., **42**, 124 (1927).

[32] Hazel and Sorum: J. Am. Chem. Soc., **52**, 1337 (1930).

[33] Kolloid-Z., **6**, 83 (1911); *cf.* Yajnik and Bhatia: J. chim. phys., **22**, 589 (1925).

[34] Z. physik. Chem., **123**, 303 (1926).

[35] Fajans and Beckerath: Z. physik. Chem., **97**, 478 (1921).

cesium and from magnesium to barium, it follows that the adsorptive power and coagulative action should increase in this direction, as the results show (p. 218).

TABLE XLIV

COAGULATION OF COLLOIDAL PRUSSIAN BLUE SOL BY ELECTROLYTES

Sol 1		Sol 2	
Electrolyte	Precipitation value millimols/l	Electrolyte	Precipitation value millimols/l
KNO_3...	40	KNO_3	80
$LiNO_3$.	130	$Mg(NO_3)_2$	5 7
$CsNO_3$	7	$Ca(NO_3)_2$	4 5
$Li_2SO_4/2$	1000	$Sr(NO_3)_2$	2 9
$K_2SO_4/2$	72	$Ba(NO_3)_2$	1 1
$Cs_2SO_4/2$	7		

In order to get a more exact insight into the relationship between adsorbability and heat of hydration, the heat of adsorption in solution, U_s, can be regarded as the small difference between the heat of adsorption in vacuum, U_v, and the heat of hydration, W, that is, $U_s = U_v - W$. According to Fajans [36] the heat of adsorption in vacuum is inversely proportional to the sum of the radius of the charged ions, r_1, and of the adsorbed discharged ions, r_2; that is,

$$U_v = \frac{K_1}{r_1 + r_2}$$

Born [37] points out that the heat of hydration includes the dielectric constant of the solution and as a first approximation is inversely proportional to the ratio of the adsorbed ions r_2; that is,

$$W = \frac{K_2}{r_2}$$

Now if K_1, r_1, and K_2 are assumed to be constant, then

$$U_s = \frac{K_1}{r_1 + r_2} - \frac{K_2}{r_2} = f(r_2)$$

[36] Verhandl. deut. physik. Ges., **21**, 549, 709, 714 (1919); Naturwissenschaften, **9**, 733 (1921).

[37] Z. Physik, **1**, 47 (1920).

On differentiation this becomes,

$$f^1(r_2) = -\frac{K_1}{(r_1 + r_2)^2} + \frac{K_2}{r_2^2} = \frac{K_2(r_1 + r_2)^2 - Kr_2^2}{r_2^2(r_1 + r_2)^2}$$

The last value comes out to be positive in the case under consideration. This means that, although the two values $K_1/(r_1 + r_2)$ and K_2/r_2 decrease with increasing radius of the adsorbed ions r_2, the difference with increasing r_2 is always positive. Accordingly, the heat of adsorption must increase in the ion series from lithium to cesium and from magnesium to barium. Some data on the heat of hydration of alkali cations and that of adsorption of the corresponding nitrates by charcoal are given in Table XLV. It will be seen that the heat of hydration

TABLE XLV

HEAT OF HYDRATION OF ALKALI IONS AND HEAT OF ADSORPTION OF ALKALI NITRATE ON CARBON

Heat of hydration of alkali ions		Molecular heat of adsorption of salts by carbon	
Ion	Heat of hydration, calories per gram ion	Salt	Heat of adsorption per mol, relative values
Li	120	$LiNO_3$	8 90
Na	92	KNO_3	10 40
K	72	$CsNO_3$	11 72
Rb	68		
Cs	62		

falls as one goes down the series, whereas the heat of adsorption of $LiNO_3$, $NaNO_3$, and KNO_3 is in the ratio 8.9 : 10.4 : 11.7. Since the heat of adsorption is a measure of the adsorbability, the increase in precipitating power from lithium to cesium is accounted for.

Although these considerations indicate the existence of a qualitative relationship between adsorption and heat of hydration in the cases under consideration, it should be emphasized that this is but one of a number of factors which determine adsorbability. Indeed, it is probable that heat of hydration of ions plays but a minor rôle in many instances. We have seen that the solubility of the salt which an ion may form with an adsorbent appears to be the important factor in the adsorption of certain ions (pp. 37, 103).

In this connection, Mukherjee [38] attributes the variation in adsorbability in a series of ions such as the alkalis to differences in their mobilities. The ions adsorbed on the particles exert an attraction on the ions of opposite sign in the solution. The latter will be held firmly so that they cannot migrate provided that their kinetic energy remains below a value U_s which is necessary to separate the ion from the oppositely charged point of the surface. The value U_s, as heretofore, is the work of adsorption or its equivalent, the heat of adsorption. According to Mukherjee, it can be calculated from the expression

$$U_s = \frac{n_1 n_2 e^2}{Dx}$$

in which n_1 is the valence of the adsorbed ion, n_2 the valence of the ion of opposite charge in the solution, e the charge on the electron, D the dielectric constant of water, and x the distance between the centers of the ions at the position of minimum distance. The value of x is therefore equal to the sum of the radii of the ions or $(r_1 + r_2)$. Born [39] showed, however, that the radius of the alkali metals increases in the series from lithium to cesium; hence, the value of U_s calculated from the above equation must decrease from lithium to cesium, which is contrary to the observations of Lachs and Lachman. Moreover, the view of Mukherjee is unsound theoretically, since adsorption represents an equilibrium condition which would not be determined solely by the mobility of the ions.[40]

The precipitation values of electrolytes decreases with dilution of sol irrespective of the valence of the precipitating ion.[41] When the activity coefficients of the cations at their respective precipitation values, $f+$, are plotted against the sol concentration, the curves tend to converge at higher concentrations (10 g/l).[41] (*Cf.* pp. 194, 318.) Dilution with alcohol likewise sensitizes the sol toward electrolytes.[42]

Action of Acids. Weir [43] found the *p*H of the supernatant liquid at the coagulation point of hydrochloric, sulfuric, and citric acids to be approximately constant at a value of 1.9; for acetic acid, it was 2.7; and for oxalic acid which exerts a strong peptizing action in dilute

[38] Phil. Mag., (6) **44**, 321 (1922).

[39] Z. Physik, **1**, 221 (1920).

[40] *Cf.* Zsigmondy: "Kolloidchemie," 5th ed., **1**, 200 (1925).

[41] Weiser and Nicholas: J. Phys. Chem., **25**, 742 (1921); Wolshin: J. Russ. Phys.-Chem. Soc., **42**, 863 (1910); Lederer: Kolloid-Z., **76**, 54 (1936).

[42] Kawamura: Hokkaido J. Med. Japan, **7**, 287 (1929).

[43] J. Chem. Soc., **127**, 2245 (1925).

solution, it was 0.9 to 0.8. Kugel,[44] studied the effect of varying concentrations of hydrochloric and sulfuric acid on the rate of agglomeration of the sol. The *p*H value was determined conductometrically just after the acid was added and at the completion of the coagulation; and the adsorption of hydrogen ion was calculated. The curves showing the effect of *p*H value on the rate of coagulation for the two acids are similar but they do not coincide. The adsorption curves are quite similar from *p*H = 2 to 5, but the sulfuric acid curve is slightly lower than the hydrochloric acid curve. This is probably experimental error since sulfate is in general more strongly adsorbed than chloride and hence, as a rule, sulfuric acid is more strongly adsorbed than hydrochloric acid.

Action of Mixtures of Electrolytes. Investigations of the precipitating action of salt pairs on Prussian blue sol led to results and conclusions similar to those already described for copper ferrocyanide sol (p. 323). Rabinerson[45] showed the existence of an antagonistic action with the pairs KCl–$BaCl_2$, NaCl–$BaCl_2$ and $BaCl_2$–$K_3Fe(CN)_6$ which was attributed to the stabilizing action of the anions. Ghosh and Dhar[46] likewise found a strong antagonistic action with the salt pair KCl–$BaCl_2$; on the other hand, with the pairs HCl–KCl and HNO_3–KNO_3, the acids exert such a marked sensitizing action that the precipitation values of mixtures falls well below the calculated additive values.

Mutual Action of Sols

If one sol is treated with a second the first will be stabilized, sensitized, or completely or partially precipitated, depending on the nature and relative concentrations of the two sols. Ghosh and Dhar[47] report that gelatin and tannic acid sensitize Prussian blue in low concentrations but stabilize it in higher concentrations. Since gelatin in acid or neutral solutions is a positive sol, small amounts would be expected to exert a sensitizing action on negative Prussian blue sol. Tannic acid, on the other hand, is a negatively charged sol and, in the absence of impurities, should have a stabilizing effect at all concentrations.

If a small amount of a positively charged sol is added to a large amount of a negatively charged sol, the former may be stabilized by adsorption on the latter, which, in turn, will be sensitized to some ex-

[44] Kolloid-Z., **51**, 240 (1930).
[45] Kolloid-Z., **42**, 50 (1927).
[46] J. Phys. Chem., **29**, 659 (1925); **30**, 842 (1926).
[47] Kolloid-Z., **44**, 218 (1928).

tent. Complete mutual coagulation takes place when the potential of each sol is lowered below the point of stability. It is claimed that this happens when electrochemical equivalent amounts of each sol are present;[48] but other factors must be taken into account (p. 215). The addition of electrolytes to the sol will widen the range of mutual coagulation as illustrated by Rabinerson[49] with positive ferric oxide sol and negative Prussian blue sol. Some typical results are shown diagrammatically in Fig. 53, in which the percentage composition of the mix-

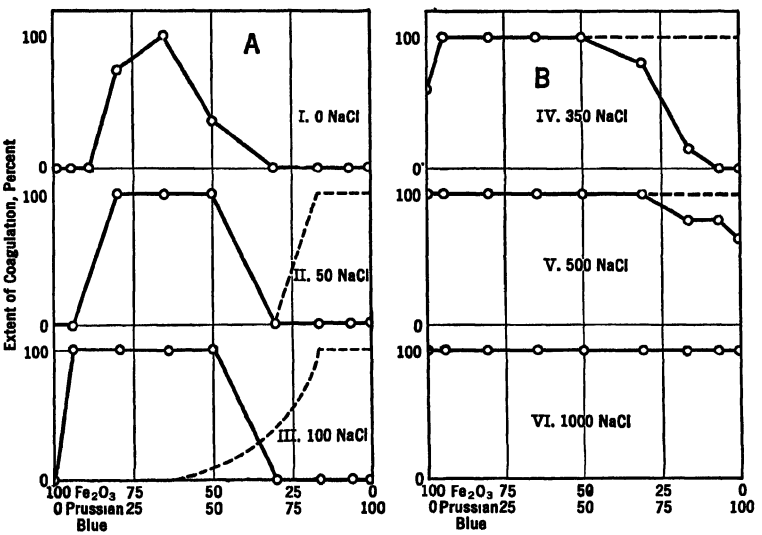


FIG. 53.—Mutual action of ferric oxide sol and Prussian blue sol in the absence and in the presence of sodium chloride. (Sodium chloride concentration in millimols per liter)

tures is plotted as abscissa against the percentage amount of coagulation as ordinate, without the addition of sodium chloride and in the presence of five different concentrations of the salt. The several unbroken curves show the effect of sodium chloride in the amounts indicated, on the mutual action of the sols. The dotted curves show the extent of coagulation by the sodium chloride of pure ferric oxide sols of the different concentrations. The ferric oxide sol is the more sensitive to the action of electrolytes, sodium chloride causing clouding of

[48] *Cf* Lottermoser and May: Kolloid-Z., **58**, 61 (1932).
[49] Kolloid-Z., **39**, 112 (1926).

the 0.1% sol at a concentration of 200 millimols/l and complete coagulation at 500, whereas a 0.05% Prussian blue sol requires 400 millimols/l for clouding and 1000 for complete coagulation.

In the absence of sodium chloride, complete mutual precipitation takes place sharply with approximately 33% Fe_2O_3 and 67% Prussian blue. Both to the right and left of this point the amount of precipitation falls off, decreasing to zero with about 90% Fe_2O_3 and 9% Prussian blue on the left, and with 28.5% Fe_2O_3 and 71% Prussian blue on the right. The presence of sodium chloride in the mixture of sols increases the range of complete precipitation both to the left and to the right. This effect is more marked with excess ferric oxide than with excess Prussian blue since the former sol is more sensitive to the action of sodium chloride. When the concentration of salt reaches 500 millimols/l, the left portion of the curve becomes parallel with the abscissa whereas the right portion takes this position only after the concentration has been raised to 1000 millimols.

The observations show quite clearly the relationships among sensitization, mutual coagulation, and protective action. It is obvious that within a certain range each sol sensitizes the other since an amount of sodium chloride which will not coagulate either sol alone will effect complete coagulation of a mixture that appears stable. For example, sols containing 95.24% Fe_2O_3 + 4.76% Prussian blue and 90.91% Fe_2O_3 + 9.09% Prussian blue do not precipitate in the absence of sodium chloride but 100 millimols/l will precipitate both mixtures, although this amount of salt does not cloud either sol taken separately. The protecting action of Prussian blue is also illustrated by the curves. For example, the dotted curves in IV disclose that the 0.1% Fe_2O_3 sol is clouded by 250 millimols/l of sodium chloride whereas the 0.2% sol is completely precipitated. On the other hand, the 0.02% sol is not even rendered cloudy by this amount of salt when Prussian blue is present in the ratio of 71.4% to 28.6% of Fe_2O_3. In general, in the region of electrolyte concentrations which lies between the coagulation value of the two sols of opposite sign, the more sensitive sol is protected by an excess of the more stable sol.

The gelatinous precipitates of the positively charged hydrous oxides or hydroxides of iron, aluminum, magnesium, thorium, and the rare earths [50] as well as barium sulfate [51] and plastic clay [52] adsorb Prussian

[50] Wedekind and Fischer: Ber, **60B**, 541, 544 (1927).
[51] Wohlers: Z. anorg. Chem., **59**, 203 (1908).
[52] Rohland: Z. anorg. Chem., **77**, 116 (1912).

blue when shaken with the sol, but the negative hydrous oxides of titanium, tungsten, and tantalum do not adsorb the color.

Hydrous ferric oxide treated with hydrocyanic acid gives a black gel which is an irreversible adsorption complex of Prussian blue and ferric oxide.[53] It is believed that the hydrocyanic acid first reduces some of the ferric oxide to ferrous oxide which dissolves in the excess acid to give hydroferrocyanic acid which then reacts with hydrous ferric oxide giving Prussian blue that is adsorbed by the remaining oxide. A black gel containing as much as 10.5% Prussian blue was prepared in this way.

[53] Wedekind and Fischer: Ber., **60B**, 541 (1927); Wedekind: Naturwissenschaften, **15**, 163 (1927).

Part V

THE COLLOIDAL SILICATES

CHAPTER XX

SILICATE SOLS AND GELS; THIXOTROPY

The most familiar examples of silicates in the colloidal state are colloidal clays and claylike bodies such as bentonite. The laboratory preparation of silicate gels and sols may be accomplished in some instances by double decomposition of sodium silicate and salts of the heavier metals. The nature of the product obtained by this process will depend not only on the heavy metal entering into the reaction but also, to a considerable extent, on the nature of the sodium silicate solutions. Accordingly some attention must be given to the constitution and properties of such solutions.[1]

Sodium Silicate Solutions

When reference is made to solutions of sodium silicate one usually thinks of water glass which is not a solution of a definite chemical individual but is a variable system of the components sodium oxide, silica, and water. In commercial silicate solutions the ratio Na_2O: SiO_2 may vary from 1 : 1 to 1 : 4; sodium metasilicate in which the ratio is 1 : 1 is on the market as a crystalline powder. From earlier measurements of conductivity[2] and freezing point,[3] it was concluded that dilute solutions of sodium silicate are practically completely hydrolyzed, yielding sodium and hydroxyl ions and colloidal hydrous silica, but no silicate ions. More recent work indicates, however, that dilute silicate solutions are hydrolyzed much less than formerly supposed and that the percentage hydrolysis is quite low in concentrated solutions. Moreover, the solutions appear to contain silicate ions which, rather than hydroxyl ions, appear to be adsorbed by colloidal silica giving the latter a negative charge. Some of the experimental evidence in support of these conclusions will now be given.

[1] *See especially* Vail: "Soluble Silicates in Industry," Am. Chem. Soc. Monograph, No 46 (1928).

[2] Kohlrausch: Z. physik Chem., **12**, 773 (1893).

[3] Loomis: Wied. Ann., **60**, 523 (1897).

Conductivity

Harman [4] prepared pure crystalline sodium metasilicate, $Na_2SiO_3 \cdot 9H_2O$, and from a solution of this salt he made solutions of varying ratios of $Na_2O : SiO_2$ by removing the alkali electrolytically.[5] Solutions in which the ratio $Na_2O : SiO_2$ was 2:1 and 1:1 were found to be excellent conductors,[6] and solutions in which the ratio was 1:2, 1:3, and 1:4 were good conductors in dilute solution but abnormally low in concentrated solution. This is illustrated graphically in Fig. 54*A*, in which the equivalent conductivity of solutions of various con-

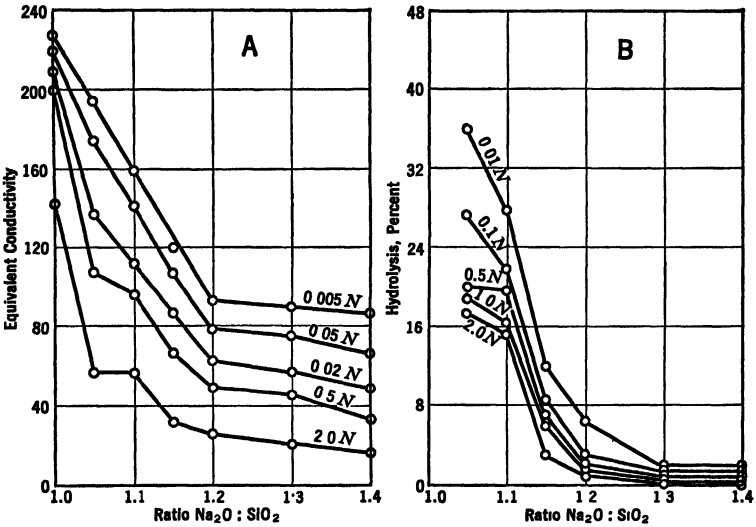


FIG. 54.—Curves for (*A*) equivalent conductivity and (*B*) percentage hydrolysis against the $Na_2O : SiO_2$ ratio for solutions of various concentrations.

centrations is plotted against the $Na_2O : SiO_2$ ratio. Considering dilute solutions, it will be seen that the conductivity of a caustic soda solution to which silica has been added decreases linearly and rapidly until the ratio 1:2 is reached, where there is a sharp change in direction, the conductivity again falling regularly and linearly but not so rapidly as the less siliceous solutions. The sharp change in direction

[4] J. Phys. Chem., **29**, 1155 (1925).

[5] Spencer and Proud: Kolloid-Z., **31**, 36 (1922); Lottermoser: **30**, 346; Kröger: 16 (1922).

[6] *Cf., also,* Kohlrausch: Wied. Ann., **17**, 756 (1892); Z. physik. Chem., **12**, 773 (1893); Kahlenberg and Lincoln: J. Phys. Chem., **2**, 77 (1898).

at the ratio 1:2 is taken to indicate the existence of a definite salt in solution. Since $Na_2SiO_3 \cdot 9H_2O$ is a well-defined crystalline salt, the absence of a break in the curve at 1:1 indicates that the salt is appreciably hydrolyzed in dilute solution and that the linear decrease in conductivity is caused by the gradual disappearance of the mobile hydroxyl ion. The conductivity for ratios up to 1:2 is much greater than could result alone from hydrolysis into sodium hydroxide and colloidal hydrous silica. Above the ratio 1:2 where the hydroxyl ion concentration is very low, the sodium ion accounts for only about one-half of the observed conductivity. To account for the remainder, the obvious way is to postulate the existence of silicate ions[7] with mobilities ranging from 40 to 60. It may be mentioned at this point that the equivalent conductivity calculated from freezing-point, hydroxyl ion, and sodium ion measurements agrees well with conductivity data determined experimentally.

The curves for more concentrated solutions exhibit three changes of direction which might be taken to indicate the presence in solutions of a salt with the $Na_2O:SiO_2$ ratio 2:1 as well as 1:1 and 1:2. But since there is no independent evidence of the existence of salts with ratios other than 1:1 and 1:2, it is probable that other ratios are mixtures of these with sodium hydroxide or hydrous silica, as the case may be. To account for the relatively low conductivity of concentrated solutions above the ratio 1:2, Harman suggests that either the extent of ionization is too low, or aggregate or colloid formation takes place. There is no doubt of the existence of colloidal particles in the more siliceous solutions.[8]

Hydrolysis

The hydrolysis of silicate solutions of varying concentrations and of varying $Na_2O:SiO_2$ ratios was determined electrometrically by Bogue,[9] whose observations were confirmed in all essential respects by Harman.[10] Harman's results are shown graphically in Fig. 54*B*, in which the percentage hydrolysis calculated from the hydroxyl ion concentration as given by hydrogen electrode measurements is plotted against the $Na_2O:SiO_2$ ratio. It will be seen that these data show the hydrolysis to be far from complete. Thus a 0.01 *N* solution of Na_2SiO_3 is hydrolyzed to the extent of 27.8% whereas ratios of 1:3

[7] *Cf., also,* Main: J. Phys. Chem., **30**, 535 (1926).
[8] Stericker: Chem. & Met. Eng., **25**, 61 (1921).
[9] J. Am. Chem. Soc., **42**, 2575 (1920).
[10] J. Phys. Chem., **30**, 1100 (1926).

and 1 : 4 at the same concentration show only 1.5% hydrolysis. Moreover, the degree of hydrolysis falls off with increasing concentration for all ratios.

It is obvious that the correctness of the conclusions concerning the percentage hydrolysis depends upon the accuracy of the determination of the hydroxyl ion concentrations. It is assumed, of course, that the hydrogen electrode measurements give a true measure of the hydroxyl ion present in the system. This is probably not the case if a part of the hydroxyl ions are adsorbed by colloidal particles present in the system. It has been demonstrated that adsorbed chloride ion will not give a test with silver nitrate [11] and its effect on a chlorine electrode will be negligible. Similarly, it is extremely improbable that adsorbed hydroxyl ion would behave toward a hydrogen electrode in the same way as a free hydroxyl ion. The values of the hydrolytic dissociation determined from electromotive force measurements on a colloidal system, such as certain sodium silicate solutions, will be correct only if no hydroxyl ion is adsorbed. As will be shown in the next section, it is not possible to account for the high osmotic activity of dilute sodium silicate solutions if it is assumed that the silica exists only as colloidal silica which has adsorbed hydroxyl ion. Accordingly, it may well be that Bogue's and Harman's determinations of percentage hydrolysis are approximately correct.

Osmotic Activity

The osmotic activity of various sodium silicate solutions has been calculated from measurements of the vapor pressure,[12] boiling point,[13] and freezing point.[14] In Fig. 55*A* are plotted Harman's data for the molecular lowering of the freezing point, Δ/m, against the Na_2O : SiO_2 ratio for solutions of varying concentrations; and in Fig. 55*B*, the corresponding activity coefficients as calculated by Harman.[15] It will be seen that ratios 2 : 1 and 1 · 1, and to a lesser degree 1 : 2, exhibit a high degree of osmotic activity especially in dilute solutions. Moreover, ratios 1 : 3 and 1 : 4 show a relatively high osmotic activity

[11] Ruer: Z. anorg. Chem, **43**, 85 (1905).

[12] Harman · J Phys. Chem., **30**, 917 (1926); Bennett: **31**, 890 (1927).

[13] Cann and Cheek. Ind Eng. Chem., **17**, 512 (1925); Cann and Gilmore: J. Phys Chem, **32**, 72 (1928).

[14] Kahlenberg and Lincoln: J. Phys. Chem., **2**, 77 (1898); Thompson: Vail's "Soluble Silicates in Industry," 42 (1928); Harman: J. Phys. Chem, **31**, 359 (1927).

[15] *Cf., however,* Randall and Cann: J. Am Chem. Soc., **50**, 347 (1928).

in dilute solutions as compared with the low value in concentrated solutions.

If the van't Hoff factor i is calculated for the solutions in which the $Na_2O : SiO_2$ ratio is 1 : 1 using the expression $i = \Delta/m \times 1.858$,[16] a fairly high degree of hydrolysis or ionization is indicated, even in the more concentrated solutions. In a 0.01 N solution, the value for i comes out to be 3.87, which lies between 3, expected if total ionic dis-

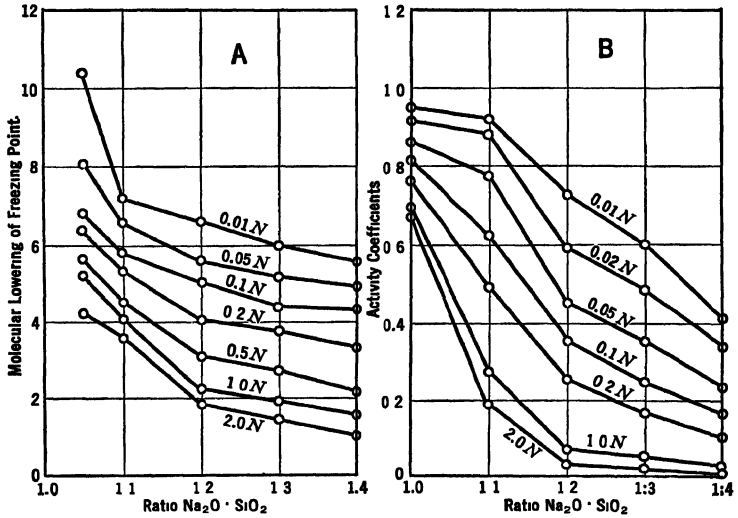


FIG 55.—Curves for (*A*) molecular lowering of the freezing point and (*B*) activity coefficient against the Na_2O SiO_2 ratio for solutions of various concentrations

sociation takes place, and 4, the consequence of total hydrolytic dissociation and ionization of the hydroxide formed, assuming in the latter event that all the silica is colloidal and without influence on the other constituent of the solution If the laws of ideal solutions are assumed to apply in this instance, the percentage hydrolysis is $3.87/4 \times 100 = 97\%$, which agrees well with the figure calculated from conductivity measurements of both Harman and Kohlrausch [2] and from the freezing-point measurements of Loomis.[3]

If the extent of hydrolysis is determined by the concentration of sodium ions,[17] and if the OH^- ions are assumed to be adsorbed to a

[16] The molecular lowering of an ideal substance at infinite dilution.

[17] Harman: J. Phys Chem., **30**, 922 (1926).

large extent by colloidal silica so that the OH^- ion concentration agrees with the percentage hydrolysis found by electromotive force measurements, Harman calculates i for 0.005 M Na_2SiO_3 to be 2.53 as compared with 3.87 from freezing-point measurements. This non-agreement, which is clearly outside the bounds of experimental error, furnishes definite evidence against OH^- ion adsorption. Harman deduced therefore that the 1 : 1 ratio is Na_2SiO_3 which undergoes both hydrolytic and ionic dissociation giving Na^+, OH^-, and SiO_3^{--} ions, and H_2SiO_3 most of which is not colloidally dispersed.

From similar considerations, Harman concludes that the solutions in which the $Na_2O : SiO_2$ ratio is 1 : 2 do not contain the salt $Na_2Si_2O_5$ but rather $NaHSiO_3$ which behaves like Na_2SiO_3 in giving rise to Na^+, OH^-, and $HSiO_3^-$ ions together with H_2SiO_3. Electrometric titration of sodium silicate solutions likewise indicates that silicic acid is a dibasic acid giving salts $NaHSiO_3$ and Na_2SiO_3.[18, 19] The 1 : 3 and 1 : 4 ratios, on the other hand, do not appear to be definite salts but rather to consist of complex aggregates and ionic micelles which are assumed tentatively to have the composition $[mSiO_3, nSiO_2aq]^{m--}$.

The ultramicroscope definitely discloses the presence of colloidal particles in the more siliceous mixtures. Since some silicate ions exist in such solutions, the colloidal particles derive their negative charge from adsorption of these ions giving what may be termed colloidal ions or ionic micelles; but such colloidal particles differ in no essential way from colloidal silver iodide particles stabilized by preferential adsorption of I^- ions or of colloidal gold particles stabilized by preferential adsorption of $AuCl_2^-$ ions.

Transport Numbers of the Ions

The transport numbers of the ions in certain silicate solutions determined by Harman[20] using the Hittorf method are given in Table XLVI. These results indicate that a fair proportion of the current, at least one-half in the most siliceous mixtures, is carried by the silica. Harman recognized two possibilities: either the silica exists as ions, or hydroxyl ions are adsorbed on colloidal particles giving the necessary charge to the silica. Since the view that the silica exists chiefly as colloidal particles that have adsorbed hydroxyl ions is incompatible

[18] Harman: J. Phys. Chem., **31**, 616 (1927).

[19] Stericker: Vail's "Soluble Silicates in Industry," 54 (1928); Joseph and Oakley: J. Chem. Soc., **127**, 2815 (1925).

[20] J. Phys. Chem., **30**, 359 (1926).

TABLE XLVI

TRANSPORT NUMBERS OF IONS IN SODIUM SILICATE SOLUTIONS

Ratio Na_2O+SiO_2	N_{Na}	$N_{silicate}$	$N_{OH}=1-(N_{Na}+N_{silicate})$
1 : 1	0 37	0.16	0 47
1 : 2	0 41	0.41	0 18
1 : 3	0.43	0.46	0.11
1 : 4	0.48	0 59	

with the high osmotic activity of dilute silicate solutions, it is concluded that the silica must exist as ions. It does not follow from this, however, that all the silicate exists as simple SiO_3^{--} or $HSiO_3^-$ ions free or adsorbed by colloidal silica. It is possible if not altogether probable that a portion at least of the SiO_3^{--} ions are present as true colloidal micelles consisting of agglomerates of ions which have a definite composition. Such colloidal ions or micelles possess a mobility comparable to that of single ions.

Diffusion

The existence of silicate ions and of crystalloidal H_2SiO_3 in silicate solutions is further indicated by diffusion experiments of Harman [19] and Ganguly [21] using membranes of collodion and parchment paper. For example, most of the silica in 0.3 *N* solutions containing Na_2O and SiO_2 in the ratio 1 : 1 and 1 : 2 was diffusible. Moreover, two-thirds of the silica in 0.3 *N* and one-third of the silica in 1 *N* solutions of the 1 : 4 ratio diffused through the membranes. In very dilute solutions of all ratios, the silica behaved as if it were in true solution. This was confirmed by testing for silicate ion colorimetrically,[22] using a test which depends on the formation of greenish yellow silicomolybdate.[23]

Although the work of Harman [24] and others has furthered our knowledge of the nature of sodium silicate solutions, one is left with the impression that an important factor in the behavior of such solutions is not taken into account, namely the effect of aging. Mylius and Groschuff [25] are of the opinion that, at the moment of its formation

[21] J. Phys. Chem., **31**, 407 (1927).
[22] Harman: J. Phys. Chem., **31**, 622 (1927).
[23] Dienert and Waldenbulcke: Bull. soc. chim., (4) **33**, 1131 (1923).
[24] *Cf.* J. Phys. Chem., **32**, 44 (1928).
[25] Ber., **39**, 116 (1906).

from water glass, silicic acid exists as such in a molecular solution which passes unchanged through a dialyzing membrane; and that the colloidal state results from polymerization of the acid with the splitting off of water. In commenting on this view some years ago,[26] it was suggested that newly formed silicic acid is colloidal but the primary particles are too finely divided to be stopped by the membrane employed; but, after a time, these very highly dispersed particles coalesce to form larger primary particles with the loss of adsorbed water as a result of the decrease in specific surface. In the light of Harman's work, it now appears that silicic acid, as such, exists in solution as Mylius and Groschuff assumed; moreover such a solution goes over in time to the colloidal state and the particles of colloidal silica agglomerate and age slowly but continuously,[27, 28] approaching crystalline SiO_2 as a limit.[29, 27] So far as the author is aware, the experiment has not been tried, but one might expect to find ultramicrons even in dilute solutions of the definite salt Na_2SiO_3, if the solutions were allowed to stand for a long time. Since everybody recognizes the existence of colloidal silica in more siliceous solutions, it is obvious that the system when first prepared is not in equilibrium, attaining the condition only after long standing, if at all. The tendency of colloidal silica particles to coalesce into larger aggregates, and finally to gel, is clearly recognized by Vail [30] as one of the outstanding characteristics of silicate solutions containing colloidal silica.

Silicate Gels

When solutions not too dilute of sodium silicate and the salt of a heavy metal are allowed to interact, a gelatinous precipitate is obtained which varies in composition depending on the $Na_2O : SiO_2$ ratio in the silicate solution, the nature of the metal, the concentration of the solutions, and the relative proportions of the reacting materials. Jordis and collaborators [31] have made a careful study of the reactions between solutions of sodium metasilicate and copper sulfate, ferrous sulfate, and ferric chloride, with the following results:

[26] Weiser: "The Hydrous Oxides," 194 (1926).

[27] *Cf* Schwarz and Stowener: Kolloid-Beihefte, **19**, 171 (1924)

[28] *Cf.* Schwarz and Liede: Ber., **53B**, 1509, 1680 (1920); Schwarz Kolloid-Z, **28**, 77 (1921); Grundmann: Kolloid-Beihefte, **18**, 197 (1923).

[29] *Cf* Bachmann· Z anorg. Chem, **100**, 1 (1917); Zsigmondy-Spear· "Chemistry of Colloids," 137 (1917).

[30] J. Soc. Chem. Ind., **44**, 214*T* (1925).

[31] Jordis and Hennis: J prakt Chem, (2) **77**, 240 (1908); Jordis: Z angew. Chem., **21** II, 1982 (1908).

Copper metasilicate occurs in nature and may be prepared in a definitely crystalline form by placing cupric nitrate and potassium silicate on opposite sides of a permeable membrane which allows slow diffusion [32] and at the same time holds the colloidal constituents in the silicate solution. On rapid mixing of equal amounts of 0.1 *M* solutions of copper sulfate and sodium metasilicate, the resulting gel contained all the copper but between 3.5 and 4.75% of the silicate remained in solution. When the amount of silicate was doubled, the additional silicate did not all remain in solution, which contained but 43.8% instead of the expected 54%. Equal amounts of *N* $CuSO_4$ and *N* $Na_2O \cdot 2SiO_2$ gave a gel which contained all but 4.5% of the total SiO_2. The gel developed microscopic green crystals, probably of $CuSiO_3$, on standing. Since the aqueous suspension of copper hydroxide turns black on boiling and that of the gel does not, it is claimed that the latter consists essentially of copper silicate rather than a mixture of hydrous copper hydroxide and silica. This does not follow since the blue copper hydroxide is stabilized by various substances (Vol. II, p. 151) and silica may well be one of them.

Ferrous sulfate behaves toward silicate solutions like copper sulfate, and some ferrous silicate may form. Ferric and aluminum salts, on the other hand, give mixtures of the respective hydrous metallic oxides and hydrous silica.

Britton [33] has followed electrometrically the course of the reaction when 100 cc of solutions of various metallic salts were treated with a solution of $Na_2O \cdot 2.16SiO_2$ that was 0.051 *M* with respect to NaOH. In Table XLVII are given the solutions titrated, the *p*H value and the amount of silicate required to start precipitation, and the *p*H value at which the respective hydrous oxides or hydroxides precipitate. The titration curves are given in Fig. 56. The point of beginning precipitation is indicated by a short vertical line cutting the curve. In each reaction 39 cc of alkali silicate give alkali corresponding to 100 cc of salt solution. The curves lying beyond 39 cc give the effect of increasing amounts of sodium silicate on the *p*H value of the mother liquor. Some measure of the amounts of silica remaining in solution and hence of the amounts carried down with the respective metallic oxides or hydroxides was obtained by following the *p*H change when 0.051 *M* $Na_2O \cdot 2.16SiO_2$ was added to 139 cc of solution containing the same concentration of neutral sodium salt as the original mother liquors, but with different amounts of silica. Thus, curve I in Fig. 56 gives the

[32] Becquerel. Compt. rend., **67**, 1081 (1868).

[33] J. Chem. Soc., 425 (1927).

change in pH when the sodium silicate is added to 139 cc of solution containing 39 cc of sodium silicate exactly neutralized with hydro-

TABLE XLVII

TITRATION OF METALLIC SALTS WITH 0 051 M $Na_2O \cdot 2.16SiO_2$

Solutions titrated 100 cc	Precipitation began		Corresponding oxide or hydroxide precipitates at pH
	at pH	with cc of silicate	
0 01 M $ZrCl_4$	3.98	35.0	1 86
0 01 M $ThCl_4$	3.50	30 0	3.50
0.067 M $Al_2(SO_4)_3$	4 04	5.0	4 14
0 02 M $BeSO_4$	5 31	20.0	5 69
0 02 M $ZnSO_4$	5.25	1 0	5 20
0 02 M $MnCl_2$	7 35	1 0	8 41
0 02 M $MgSO_4$	9 50	1 0	10.49
0 02 M $CaCl_2$	10 07	3 0	...

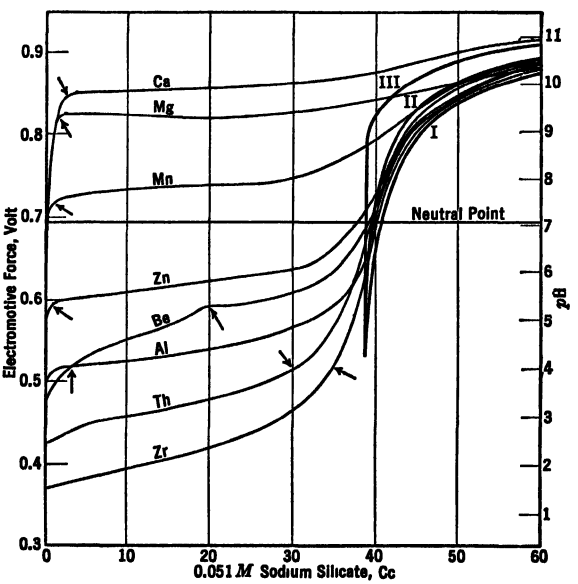


FIG. 56.—Electrometric titration curves for metallic salts with 0.051 M $Na_2O \cdot 2.16SiO_2$.

chloric acid. This curve would have been obtained if the oxides or hydroxides alone had precipitated and all the silica had remained in solution. Curve II shows the variation in *p*H which would have been produced if the metasilicates had been precipitated and the remainder of the silica had been left in solution. And curve III corresponds to the change in *p*H which would have occurred if all the silica in the 39 cc had been precipitated. Except for the curve for calcium, the portion of all curves corresponding to an excess of sodium silicate lies between curves I and II; hence the amounts of silica carried down by the various precipitates were smaller than that required to form the normal metasilicates (*cf.* p. 363). Britton interprets the calcium curve to mean that calcium silicate is formed, the high *p*H value after the addition of 39 cc of sodium silicate resulting from (*a*) hydrolysis of the calcium salt and (*b*) hydrolytic adsorption of silicate from the excess of reagent. All the other precipitates were believed to be mixtures of oxides rather than combinations to give silicates, but the possibility of some silicate formation with certain metals has not been excluded. In general, one might expect the gel to contain considerable silicate with salts of the alkaline earths;[34] some silicate with salts of copper, cobalt, and nickel;[35] and little or no silicate with salts of ferric iron, chromium, and aluminum. With the last group of salts, the gelatinous mass will probably consist almost entirely of hydrous oxides of the trivalent metal and hydrous silica.

The gels formed on mixing water glass and solutions of the chlorides of aluminum, chromium, calcium, copper, and nickel readily part with the metallic oxide, leaving pure silica on treating the dried preparations with hydrochloric acid.[36] By this procedure a silica gel with superior adsorbing qualities may be prepared.

Lloyd[37] prepared from fuller's earth an aluminum silicate gel which adsorbs alkaloids strongly from either neutral or acid solutions; the adsorbed alkaloid may be recovered by treatment with an alkaloid solvent. It has been suggested that the material be called Lloyd's reagent.[38]

The base-exchange phenomena in silicate gels both natural and synthetic will be considered in Chapter XXI.

[34] Jordis and Kanter: Z. anorg. Chem., **35**, 90, 344 (1903); **42**, 419 (1904); **43**, 48, 314 (1905); Le Chatelier· "Recherches expérimentales sur la constitution des mortieres hydraliques," Paris (1887).

[35] Schwarz and Mathis: Z. anorg. Chem., **126**, 55 (1923).

[36] Holmes and Anderson: Ind. Eng. Chem., **17**, 280 (1925).

[37] U. S. Pat. 1,048,712 (1912).

[38] Waldbott: J. Am. Chem. Soc., **35**, 837 (1913).

The "Silicate Garden"

When small crystals of various readily soluble salts such as cobalt nitrate, copper sulfate, ferrous sulfate, nickel sulfate, manganese sulfate, zinc sulfate, or cadmium nitrate are dropped into a silicate of soda solution of the right concentration and alkalinity, growths resembling plant-shoots spring up, giving rise to the so-called "silicate garden," "artificial vegetation," or "colloidal forest." [39] When the soluble crystal comes in contact with the silicate solution, it is quickly surrounded by a semipermeable siliceous gel. Diffusion then takes place through the gel membrane producing pressure inside the envelope which is distorted or broken depending on the rigidity of the structure which, in turn, depends on the concentration of the silicate solution and the nature of the metallic salt. The water which passes through the membrane dissolves more salt, and a new wall is formed around the extruded solution. This process continues, giving rise to a great variety of curious shapes and forms which differ markedly with different metals; for example, hair-like filaments result with cadmium salts, and thick fungoid growths with nickel salts. The development of the plant-like shoots is more rapid in dilute than in concentrated silicate solutions up to the point where the gel is not sufficiently rigid to retain its form, and is more rapid in solutions where the Na_2O to SiO_2 ratio is high than in the more siliceous solutions. The gels consist of the hydrous oxides of the metals and hydrous silica [40] or of a mixture of these with hydrous metallic silicates.

Silicate Sols

A stable silicate sol is best prepared by shaking a soft clay with water preferably in the presence of small amounts of electrolytes with strongly adsorbed anions such as alkali hydroxide, carbonate, or silicate which exert a marked peptizing or deflocculating action. The negatively charged particles of the clay sol are readily flocculated by electrolytes with strongly adsorbed cations. The properties of the clay sols will be discussed in Chapter XXII.

Ota and Noda [41] synthesized what they called silicate sols by the addition of a dilute water glass solution to dilute solutions of salts of

[39] Bottger: J. prakt Chem., **10**, 60 (1837); Mulder: **22**, 41 (1841); Dollfus: Compt. rend., **143**, 1148 (1906); Ross: Proc. Roy. Soc, New S. Wales, **44**, 583 (1910); J. Chem. Soc., **102** (2), 49 (1912); Krug: U. S. Pat 1,584,779 (1926).

[40] Fordham and Tyson: J. Chem. Soc., 483 (1937).

[41] J. Sci. Agr. Soc (Japan), **258**, 287 (1924).

copper, silver, magnesium, zinc, aluminum, titanium, manganese, ferrous iron, and cobalt. Although a part of the colloidal material in such preparations may be the metallic silicate, such salts will hydrolyze to a greater or lesser extent, giving a mixture of the hydrous oxide of the metal and hydrous silica. It seems altogether unlikely, for example, that any titanium silicate should exist in contact with water.

The colloidal mixtures of silicates and hydrous oxides exert an enzymic action like an oxidase when examined by the indophenol reaction. The order of activity of the silicate sols is: Ag > Cu > Co > Ti > Al > Mn > Zn > Mg > Fe^{++}. Powdered kaolin, talc, and serpentine do not exhibit this action. This behavior recalls the oxidase-like action of colloidal manganese dioxide toward guiac tincture, hydroquinone, etc. (Vol. II, p. 332).

THIXOTROPY

If a suitable amount of electrolyte is added to a fairly strong ferric oxide, chromic oxide, or alumina sol and the mixture is allowed to stand quietly, it will set to a jelly which is no more cloudy than the original sol. If the resulting jelly is shaken, a sol is re-formed which will set again on standing; and the process may be repeated as often as desired. This isothermal reversible sol-gel transformation has been termed [42] thixotropy which is derived from the Greek and means literally "to change by touching." Since the phenomenon is often encountered among the hydrous oxide systems, frequent reference is made to it in Volume II of this series.

The reversible transformation of a true inorganic sol to a true gel is, as Freundlich [43] points out, a specially characteristic and limiting case of thixotropy. This term also includes some related phenomena where the sol and gel may not be sol and gel in the true sense of the words, *i.e.*, contain only ultramicroscopic particles. For example, suspensions of clay and claylike substances such as bentonite, which contain much larger particles, may exhibit marked thixotropic behavior under certain conditions. Because of the importance of this behavior both in theory and in application, it will be considered in some detail.

Factors Determining Thixotropic Behavior

Mutual Attraction and Repulsion. The particles of a sol do not, in general, come in contact, because the magnitude and the like sign of the ζ-potential exert a repelling action which keeps them apart.

[42] Peterfi: Arch. Entwicklungsmech. Organ., **112**, 660 (1927).

[43] "Thixotropy," Hermann et Cie, Paris, 3 (1935).

But, if the potential on the particles is lowered by the careful addition of a coagulating electrolyte, a point is reached where the repelling action is just insufficient to prevent their adhesion when standing quietly. If the sol is sufficiently strong, the adhering particles form an enmeshing network structure which entrains the liquid phase, giving a jelly. Shaking breaks up the jelly structure again, giving the instable sol which will set once more on standing. Since a concentrated sol may be rendered thixotropic by adding electrolyte just short of coagulation, one should expect to find a close relationship between thixotropy of concentrated systems and the coagulation of more dilute systems. This is illustrated by the data for iron oxide sols given in Table XLVIII.[44] As a measure of the thixotropy of the concentrated sol

TABLE XLVIII

COMPARISON OF THIXOTROPY AND COAGULATION

Electrolyte	C_t 52.6 g Fe_2O_3/l	C_c 4 92 g Fe_2O_3/l
NaCl	45 0	325 0
KCl	45 0	350 0
KBr	62 0	500 0
NaOH	18 0	6 5
Na_2SO_4	12 0	3 25
$Na_2C_2O_4$	9 5	2.75
K_3-citrate	7.0	1.7

(52.6 g Fe_2O_3/l) is given the concentration C_t in millimols per liter of the several electrolytes which will cause it to set to a jelly in 400 seconds; and as a measure of the coagulation concentration of the dilute sol is given the concentration C_c in millimols per liter which will cause complete coagulation. It will be seen that for both phenomena the order of electrolytes is the same and that the valence of the anion has the usual marked effect on the positive sols.

The time of set is a measure of the time required for a sufficiently large number of particles to come in sufficiently close contact that the attractive forces cause them to adhere into an enmeshing network that entrains the liquid phase. It is still an open question[45] whether in the

[44] Freundlich and Söllner: Kolloid-Z., **45**, 348 (1928).

[45] *Cf.* Heller: Kolloid-Z., **50**, 125 (1930); Compt. rend., **202**, 61, 1507 (1936).

set jelly all the particles are fixed and motionless or whether the coherence of only a fraction of the particles furnishes a network that encloses a more dilute sol phase. The latter view seems to be favored theoretically,[46] but microscopic and ultramicroscopic observations on a thixotropic ferric oxide jelly indicate that all the particles are motionless.[47] However this may be, the phenomena of thixotropy, coagulation, and adhesion can be explained only by assuming far-reaching attractive forces. [48] As an illustration Freundlich[49] made the following calculation: Bentonite appears to consist of rod-shaped or plate-like particles having the average dimensions of $1:0.1:0.01\ \mu$. In a thixotropic paste made by mixing 1 g of bentonite with 7 cc of water, one particle will bind 4.7×10^8 water molecules. Assuming that all particles contribute to the solidification of the sol,[50] the average distance between two particles would be 100 mμ. Under such circumstances the attraction which holds the particles together cannot be classical van der Waals forces since, according to the theory, these decrease with the sixth power of the distance and so operate only at very small distances, not greater than the dimensions of a molecule. An extension of this theory by London,[51] based on the quantum mechanics, suggests that the attractive force between two molecules would also decrease with a high negative power of the mutual distance r, *e.g.*, proportional to $(1/r)^6$; but that the forces have an additive behavior. On the basis of London's theory Kallmann and Willstätter[52] calculated that the attraction between large particles containing a large number of molecules may operate at much greater distances, *e.g.*, they may decrease with the negative second power of the mutual distance.

In hydrophobic sols, the repulsive forces resulting from the double layers of ions surrounding the particles decrease according to e^{-kr}, where k, a constant used by Debye in his theory of strong electrolytes, is a function of the concentration of the electrolyte present and the valence of the ions.

From these considerations the relationship between adhesion, coagulation, and thixotropy may be represented diagrammatically as in

[46] *Cf.* Usher: Proc. Roy. Soc. (London), **125A**, 143 (1929); Kuhn: Z. physik. Chem., **A161**, 26 (1932); Bary: Compt. rend., **196**, 183 (1933).

[47] Szegvari and Schalek: Kolloid-Z., **32**, 318; **33**, 326 (1923).

[48] *Cf.* Buzágh: Kolloid-Z., **51**, 105, 230; **52**, 46 (1930).

[49] Kolloid-Z., **46**, 289 (1928).

[50] *Cf.* Hauser: Kolloid-Z., **48**, 57 (1929).

[51] Z. physik. Chem., **B11**, 222 (1931); Trans. Faraday Soc., **33**, 8 (1937).

[52] Naturwissenschaften, **20**, 952 (1932).

Fig. 57, constructed by Freundlich [53] from calculations of Rubin. The abscissa r is the mutual distance between two particles, and the ordinate

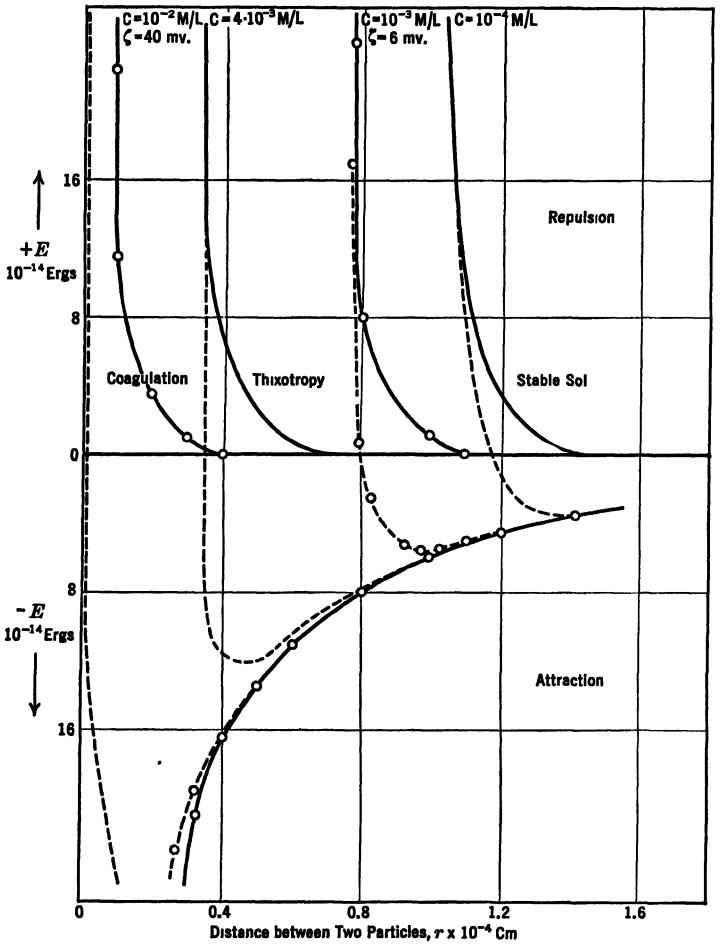


FIG. 57—Curve showing the relationship between adhesion, coagulation, and thixotropy.

is the potential energy of the repelling forces $+E$ and the attracting forces $-E$. The curve of attraction extends with small but appre-

[53] "Thixotropy," 13 (1936); *cf.* Hamaker: Rec. trav. chim., **55**, 1015 (1936); **56**, 1 (1937).

ciable values up to about 1 μ. The upper four continuous curves represent the potential energy of repelling forces at four different concentrations of potassium chloride. The distance to which such forces are effective diminishes with increasing electrolyte concentration. To test whether an equilibrium exists between attracting and repelling forces, the corresponding values of potential energy are shown in the broken curves 1, 2, 3, and 4. If a curve of this kind has a minimum, it means that an equilibrium exists between the two forces for the value of r which corresponds to the minimum. The absence of a minimum in curve 1 shows that the repelling forces predominate and a stable sol exists. The minimum value in curve 2 is not well defined, but in curve 3 it lies at a value of $r = 0.5\ \mu$. Accordingly, a large amount of liquid exists between the particles, and the equilibrium system whose particles are motionless because of the balance between the repelling and attractive forces constitutes a thixotropic gel. In curve 4 the minimum value is found at such a small value of r that but little liquid is enclosed between the particles, as in the coagulum from a sol.

The relationships among sol stability, thixotropy, and electrolyte coagulation are apparently more complicated than the potential curves of Fig. 57 would suggest. Hamaker[54] recognizes four different types of potential curves considered as a superposition of London-van der Waals attraction and electric repulsion. The curves shown diagrammatically in Fig. 58 represent energies, and consequently the slope of the curves represent forces. Corresponding curves of similar shapes may be drawn in which the slopes represent energies. In curve 1 of Fig. 58 the attractive force predominates over the repulsive force whatever the distance between the particles; in curve 2, the reverse of 1, the electric repulsion is stronger everywhere than the London-van der Waals attraction; in curve 3, intermediate between 1 and 2, the repulsive force is greatest when the particles are separated by a large distance but the attraction predominates when they are close together; and in curve 4, the reverse of 3, the attraction is strongest at large distances and the repulsion predominates at small distances.

The conditions represented by curve 3 probably obtain with most sols, but curve 2 may represent the conditions in special cases. This point of view enables one to account for reversible and irreversible coagulation: Starting with a stable sol for which curve 3 holds and adding sufficient electrolyte, the electric repulsion is reduced and the curve assumes the shape of curve 1 which causes rapid coagulation. By dialyzing the flocculated sol, the potential is restored to its original

[54] Rec. trav. chim., **55**, 1015 (1936); **56**, 1 (1937).

value but the gel will not be restored to its original stable condition since the energy minimum F will keep the particles in contact in the same way as the maximum S kept them apart. On the other hand, by starting with a stable sol for which curve 2 is valid and adding electrolytes, the curve may assume the form of type 3 and finally of type 1 which leads to flocculation. Upon dialyzing the floc, the same set of

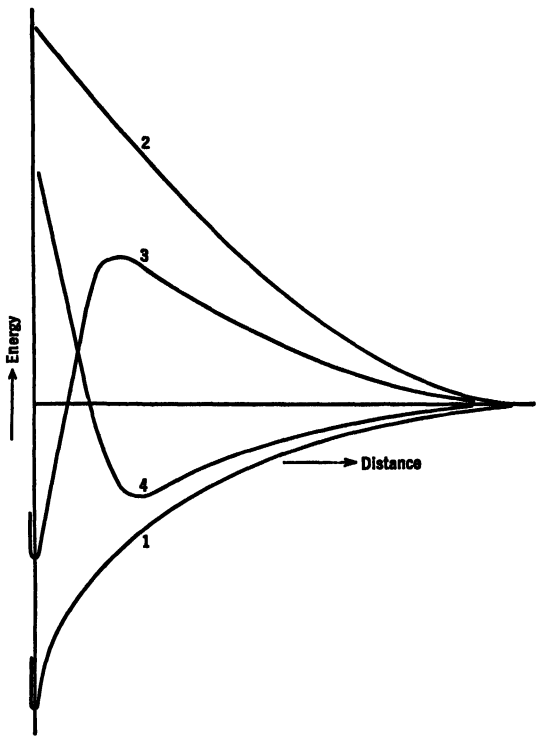


FIG. 58.—Types of potential curves.

curves is passed in the reverse direction with the ultimate peptization of the coagulum.

Curves 3 and 4 represent intermediate cases between 1 and 2, but it cannot be predicted which will be valid in a given system. Referring to Fig. 57 again, it will be seen that the transition between the lowest and highest type of curve is given by a set of curves of type 4. Hamaker points out that Freundlich has failed to recognize the possi-

bility of an equivalent though somewhat more complicated curve 3. If this shape of curve is also taken into account, it greatly complicates the consideration of the whole system. Thus, curves of either type 4 or type 3 may explain thixotropy. Those of type 3 may be useful also in accounting for thixolability, thixotropic systems of very low stability, such as has been observed with an alumina system.[55]

Hydration. The formation of a water hull around the particles is believed by Freundlich[56] to be of far more significance for thixotropic behavior than is an equilibrium between electrical and London-van der Waals forces. In support of this, thixotropic pastes have been made of mercaptobenzothiazol and such liquids as benzene, toluene, and gasoline where electrical influences are largely absent.[57] The thixotropy is attributed to adsorption of a rather thick layer of liquid, giving quasi-fluid particles which occupy enough volume so that interference is sufficient to induce gelation. Kistler[58] assumes some form of oriented anisotropy of the water, probably chains of water molecules which extend out from the surface of each particle and tend to link it with neighboring particles.

Although hydration, or more generally solvation, may influence thixotropic behavior in certain instances, Hauser[59, 60, 61] and collaborators reject the water-hull theory of thixotropy in bentonite-water systems on several grounds: (1) Since gelation occurs with very dilute suspensions (less that 1% in some instances) the hydration theory would require the formation of water hulls around the particles many molecules thick, which seems unlikely. (2) Bentonite gels possess a tensile strength which is difficult to explain on the basis of particles with adsorbed layers of water touching each other.[62] (3) The rate of gelation increases with increasing temperature, contrary to the expected behavior if water hulls are formed, since hydration usually falls off with rising temperature. (4) The addition of alcohol, a dehydrating agent

[55] Freundlich and Bircumshaw: Kolloid-Z., **40**, 21 (1926).

[56] Freundlich and Schalek: Z. physik. Chem., **108**, 153 (1923); *cf.* Ostwald: Kolloid-Z, **250** (1928); Hauser: **48**, 57 (1929); Deutsch: Z. physik. Chem., **A150**, 161 (1930); Werner: Ber., **62B**, 1525 (1929); *cf., also,* Buzágh: Kolloid-Z., **51**, 105 (1930).

[57] Recklinghausen: Kolloid-Z., **60**, 34 (1932).

[58] J. Phys. Chem., **35**, 815 (1931).

[59] J. Rheol, **2**, 5 (1931).

[60] Hauser and Reed: J. Phys. Chem., **41**, 911 (1937).

[61] Broughton and Squires: J. Phys. Chem., **40**, 1041 (1936).

[62] Lewis, Squires, and Thompson: Trans. Am. Inst. Mining Met. Engg., **118**, 1 (1936).

for hydrous colloids, changes the setting time of a bentonite suspension but slightly instead of greatly increasing it, whereas addition of water in equal amounts by volume increases indefinitely the time of setting.

Size and Shape of Particles. The particle size must be below a certain limit for a system to show thixotropic behavior.[63] With Solnhofen slate, for example, Freundlich and Juliusburger[64] found that a certain percentage of the particles must have a diameter of 1 μ and less; if the mass contained particles with diameters of 10 μ and more, the system was not thixotropic. Similarly, centrifuged suspensions of bentonite will give dispersions which show thixotropy at concentrations of 1% or lower, whereas ordinary bentonite from which the larger particles have not been removed by centrifuging must have a concentration above 4%.[65]

The shape of the particles is likewise of great importance for thixotropic behavior. Hauser[66] contends that a non-spherical shape is essential for the manifestation of true thixotropy. In line with this, it appears that the particles are rod-shaped in the thixotropic sols of vanadium pentoxide,[67] benzopurpurin, cotton yellow GX,[68] dibenzoyl cystine,[69] barium malonate,[70] and iron oxide;[71] and plate-like in the thixotropic pastes of bentonite[62, 61] and clay.[72] Moreover, a Crum's alumina sol (Vol. II, p. 105) is thixotropic[73] only when it exhibits streaming double refraction, a phenomenon resulting from orientation of non-spherical particles. On the other hand, an alumina sol may be prepared which is thixotropic but which does not show streaming double refraction, possibly because a lesser asymmetry of particles is necessary for thixotropy than for streaming double refraction.

The gelation of bentonite is visualized by Lewis, Squires, and Thompson[62, 61] as follows: the particles are assumed to be flat plates

[63] Freundlich: "Thixotropy" (1935); Russell: Proc Roy Soc (London), **154A**, 550; Russell and Rideal: 540 (1936).

[64] Trans Faraday Soc, **30**, 333 (1934); **31**, 769 (1935).

[65] *Cf.* Broughton and Squires. J. Phys Chem., **40**, 1041; Hauser and Reed: 1169 (1936); **41**, 911 (1937).

[66] J. Rheol., **2**, 5 (1931).

[67] Freundlich and Schalek: Z. physik. Chem., **108**, 153 (1924); Jochims: Kolloid-Z., **41**, 215 (1927); Rabinerson: **68**, 305 (1934).

[68] Kuhn and Erdos: Kolloid-Z., **70**, 241 (1935).

[69] Papkova-Kwitzel: Kolloid-Z, **69**, 57 (1934).

[70] Zocher and Albu: Kolloid-Z., **46**, 27 (1928).

[71] Kandelaky: Kolloid-Z., **74**, 200 (1936).

[72] Jeppesen: Kolloid-Z., **57**, 175 (1931).

[73] Freundlich and Bircumshaw: Kolloid-Z., **40**, 19 (1926); Aschenbrenner: Z. physik. Chem., **127**, 415 (1927).

which become loosely packed in three-dimensional random orientation, edge touching edge in such a way that movement is impossible and a solid "house of cards" gel structure is built up. Since gelation takes place at concentrations of bentonite as low as 0.1%, it is necessary for interference between particles to assume that their length and width is much greater than their thickness, the ratio between these dimensions being of the order of 1000–2000 to 1. Ultramicroscopic examination fails to support the assumption that such ratios exist.[74] The view that bentonite particles consist of plates of microscopic thickness and macroscopic length and width was put forward by Wherry[75] on microscopic grounds although direct microscopic evidence is lacking. The results of x-ray analysis[76] indicate that bentonite clays consist of silica and gibbsite layers separated by water, the spacing due to this separation depending on the water content of the bentonite. In the presence of a large excess of water it is possible that the plates actually break away from each other and behave as plates of molecular or colloidal dimensions. The view that gelation is due to mechanical packing of plate-like particles might account for gelation of concentrated bentonite suspensions, but it is inadequate to explain the phenomenon in extremely dilute suspensions.

Thixotropy of Bentonite and Clays

Thixotropic Behavior

Bentonite is a claylike material probably of volcanic origin found largely in Wyoming. The mineral montmorillonite is its chief constituent. This may be formulated $Al_2O_3 \cdot CaO \cdot 5SiO_2$,[77] but it contains exchangeable cations other than calcium (magnesium, sodium, potassium, etc.). Electrodialysis of bentonite removes most of the metallic cations and replaces them with hydrogen, giving a hydrogen bentonite. The direction of the streaming double refraction of bentonite suspensions[78] is changed from negative to positive[79] by electrodialysis, indicating that the exchangeable cations are a part of the crystal structure of the bentonite.[80]

After hydrogen bentonite is dried, it does not give thixotropic sus-

[74] *Cf* Hauser and Reed: J. Phys. Chem., **41**, 911 (1937)
[75] Am. Mineral., **10**, 120 (1925).
[76] Marshall: Science Progress, **30**, 422 (1936).
[77] Ross and Shannon: J. Am. Ceram. Soc., **9**, 77 (1926).
[78] Buzágh: Kolloid-Z., **47**, 223 (1929).
[79] Bradfield and Zocher: Kolloid-Z., **47**, 223 (1929).
[80] *Cf., however,* Hofmann, Endell, and Wilm: Z. Krist., **86**, 340 (1933).

pensions or pastes, but the dried clay may be converted into the original thixotropic bentonite by treating with solutions containing the cations removed by electrodialysis. Bentonite swells in water and aqueous solutions, a phenomenon closely related to its thixotropic behavior. A hydrogen bentonite or an alkali-metal bentonite swells much less than a natural bentonite.

As already pointed out, suspensions containing as little as 1% of a natural bentonite are thixotropic provided an optimum particle size is obtained by removing the larger particles with the centrifuge. Indeed, Hauser and Reed [81, 60] report evidences of gel structure at concentrations as low as 0.01–0.05% by weight in the low colloidal range. The most common method of measuring thixotropy is to determine the time which elapses after shaking the suspension in a sealed tube until it no longer runs on inverting the tube. Since thixotropic systems exhibit plastic flow, that is, they possess a definite yield value, the shape and size of the tube will influence the setting time.[61] In order to follow the rate of gelation, Freundlich and Rawitzer [82] and Price-Jones [83] determined the tensile strength and Broughton and Squires [61] measured the viscosity by the falling-ball method. The latter found that the setting time obtained by the inverted-tube method gives comparative results provided care is taken in manipulation and the diameter of the tube is kept constant. To eliminate the effect of variation of procedure in inverting the tube, Hauser and Reed [60] designed an inverting apparatus which they call a physical pendulum thixotrometer. The advantage of a procedure such as the falling-ball method is that it gives the whole of the gelation-time curve and not simply one point.

Effect of Electrolytes. As we have seen, the addition of electrolytes to hydrous oxide sols is essential to induce thixotropic behavior, and the valence of the ion opposite in charge to that on the sol is a predominating factor. Electrolytes must be added to hydrogen bentonite suspensions also in order to render them appreciably thixotropic, but the two systems are not comparable. Freundlich [84] believes that thixotropy of bentonite compounds is correlated with their degree of dissociation. Bentonite may be considered as a colloidal electrolyte

[81] J Am. Chem Soc, **58**, 1822 (1936).

[82] Freundlich and Rawitzer· Kolloid-Beihefte, **25**, 231 (1927); Hauser: Kolloid-Z, **48**, 57 (1929).

[83] J. Oil Colour Chem Assoc, **17**, 305 (1934).

[84] Freundlich: Kolloid-Z, **46**, 290 (1928); Freundlich, Schmidt and Lindau: Z physik Chem. (Bodenstein-Festband), 333 (1931); Kolloid-Beihefte, **36**, 43 (1932); Freundlich: "Thixotropy," 34 (1935).

consisting of large anionic micelles and small exchangeable cations. Only very weak thixotropic behavior is observed with the presumably weakly dissociated hydrogen bentonite whereas marked thixotropy exists with the presumably highly dissociated alkali bentonites formed by neutralizing the hydrogen compound with alkali hydroxides. Strong dissociation is believed to favor the hydration of the particles which Freundlich considers so important for inducing thixotropy.

Hauser and Reed[85] separated natural bentonite into fractions of varying particle size by means of the supercentrifuge, and determined the influence of particle size on the rate of set. The results of some observations are shown graphically in Fig. 59 for 0.85% suspensions

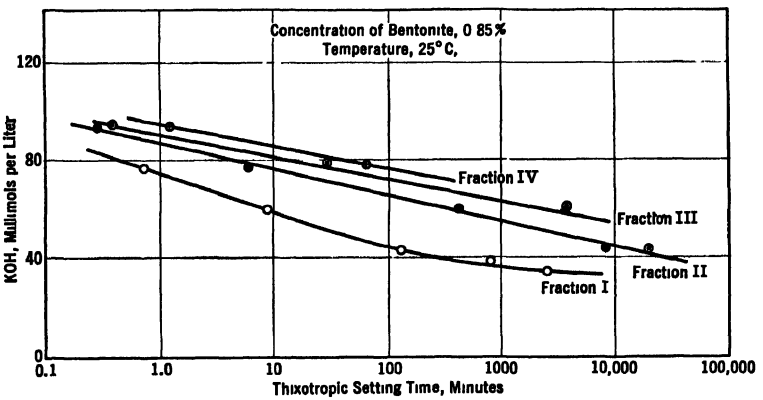


FIG 59.—Influence of particle size and alkali concentration on the thixotropic setting time of bentonite suspensions.

having the following average diameters: fraction I, 14.3 mμ; fraction II, 20.3 mμ; fraction III, 28.1 mμ; and fraction IV, 33.8 mμ. The suspensions were H-bentonites to which varying amounts of potassium hydroxide were added. In every instance, at a given concentration of base, the time required to form a gel of a given strength increases with decreasing particle size. Hauser and Reed claim that *p*H as such appears to have no particular effect on the thixotropy of bentonite (*cf.*, however, Fig. 60).

The close relationship between thixotropy and the amount of water bound or enclosed by the particles under various conditions is shown by Freundlich's observations on hydrogen bentonite pastes to which

[85] J. Phys. Chem., **40**, 1161 (1936); **41**, 911 (1937).

potassium hydroxide is added, Fig. 60. The abscissas are the logarithms of the hydroxide concentration. Curve 1 represents the setting times, curve 4 the swelling capacities, and curve 3 the sedimentation volumes. It is obvious that the optimum thixotropic behavior coincides with the maximum degree of swelling of the bentonite and the minimum volume of the sedimented material. Furthermore, curve 2, which gives the change in pH value, shows that optimum thixotropic behavior lies in the region of the neutral point and weak alkalinity.

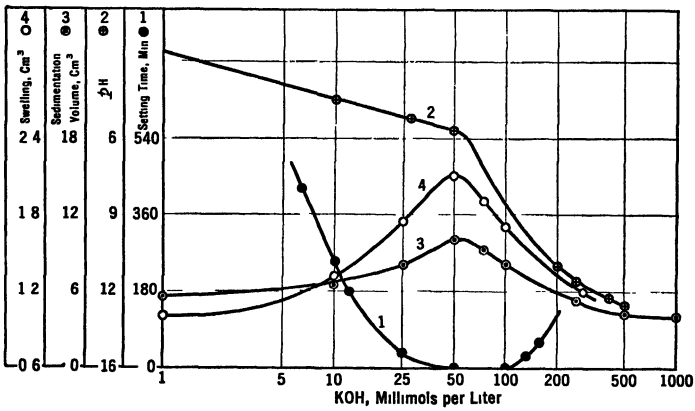


FIG. 60.—Relationship between alkali concentration and various properties of thixotropic bentonite suspensions.

Effect of Temperature. Increasing the temperature of bentonite suspensions increases greatly their rate of gelation.[61, 60] The same equation which was found by Schalek and Szegvari [86] to apply to iron oxide sols is applicable to bentonite suspensions: $\log C_t = At + B$, where C_t is the setting time, t the temperature in degrees C, and A and B are constants. The temperature coefficient A is affected by a change in the diameter of the containing vessel.

Rheopexy. Thixotropic sols containing distinct rod- or plate-like particles which set spontaneously rather slowly may be made to set rapidly by rolling the container gently between the palms of the hands or by tapping it gently in order to facilitate the orientation of the particles. For example, a vanadium pentoxide sol which sets spontaneously in 60 minutes solidified after the rolling procedure in 15 seconds. Freundlich and Juliusburger [87] have named this phenomenon

[86] Kolloid-Z., **33**, 326 (1923).

[87] Trans. Faraday Soc., **31**, 920 (1935); Juliusburger and Pirquet: **32**, 445 (1936).

rheopexy from the Greek "pectos" meaning curdled or solidified. They failed to observe rheopexy with bentonite, but Hauser and Reed [81, 60] showed that a very finely divided fraction of 1.3% bentonite which set spontaneously in 25 minutes solidified in 15 seconds after gentle tapping of the container. The effect of gentle mechanical action on the rate of gelation is well illustrated by Hauser and Reed's observations on suspensions of varying particle size, shown graphically in Fig. 61. The suspensions contained 0.85% H-bentonite to which 76.5 millimols KOH/l were added. The points on the thixotropic curve were obtained by allowing the suspensions to stand quietly. To obtain each

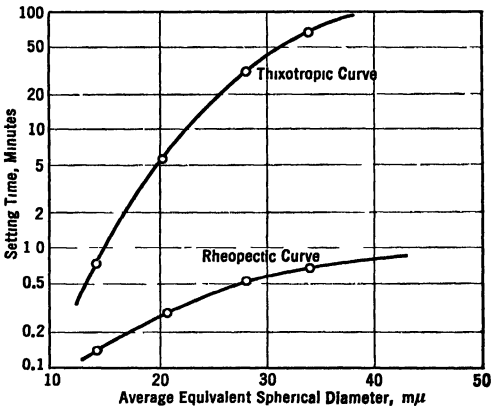


FIG. 61.—Influence of particle size on the thixotropic and rheopectic setting time of bentonite suspensions.

of the points on the rheopectic curve, the tube, 100 mm in length, which held the suspension was grasped between the thumb and third finger and was made to oscillate through an amplitude of 15–20° on each side of the vertical at the rate of 250 complete oscillations per minute. This treatment always enormously increased the rate of set; in extreme cases the mechanical motion produced gels of a given strength several hundred times faster than if the suspension were not moved.

Ultramicroscopic Observations. Hauser and Reed [60, 88] observed the ultramicroscopic changes responsible for larger-scale thixotropic behavior. On the addition of 9 milliequivalents KOH/g of dilute bentonite suspension, the individual particles were seen to cluster up forming particle clouds which in turn form a loose mass of secondary clus-

[88] *Cf.* Hauser: Kolloid-Z., **48**, 57 (1929).

ters intermeshed with channels of freely moving liquid. The particles forming the clouds showed no Brownian movement, but a few single particles remained in free motion in the channels. The application of any strong shearing force broke up the clouds and all the particles again showed Brownian motion; and the whole process was repeated on standing quietly. Gentle tapping increased the rate of formation of the clouds into more sharply defined secondary clusters—rheopetic behavior. Increasing the quantity of electrolyte caused the more rapid formation of aggregates of denser structure.

Behavior of Ordinary Clay. Concentrated suspensions of ordinary clay, kaolin, etc., behave somewhat like bentonite suspensions, but both the swelling capacity and thixotropy are much less marked. Buzágh [78] claims that suspensions of kaolin are thixotropic in the presence of alkali but not in pure water. Tamamushi [89] found that a 33⅓% kaolin is thixotropic in a neutral salt solution such as potassium chloride. Alkali solutions favor thixotropy in most clays, but some plastic clays become thixotropic when mixed with a suitable amount of pure water.[72] The particles in such thixotropic clays appear to be plate-like in shape and swell when placed in water.

Some Applications of Thixotropic Clays

Casting. The application of thixotropic clays for molding purposes should be useful in view of the facts that the volume does not change appreciably during the sol-gel transformation and thixotropy is usually closely allied to isothermal plasticity.[90] A concentrated thixotropic clay suspension will fill a mold full and may be separated from it after it has solidified. In clay casting, it appears likely that the setting of a thixotropic paste is the primary effect, the drying action of the plaster of Paris mold being of secondary importance. In practice the mixtures are always weakly alkaline, a condition favorable for thixotropy in clay pastes. Evidence is not yet available as to whether the optimum conditions for thixotropy and clay casting are similar.[91]

Thixotropic Latex. Preserved latex or concentrates of latex show no tendency to become thixotropic. The mixtures are slightly alkaline, and when bentonite is added in suitable amount it renders the whole mass thixotropic.[92] Such mixtures may be employed as a coagulant dip or for casting in molds. As an application of the former,

[89] J. Chem. Soc Japan, **57**, 132 (1936); *cf.* Kimura: **56**, 1346 (1935).
[90] Freundlich · "Thixotropy," 18 (1935); McMillen: J. Rheol., **3**, 163 (1932).
[91] *Cf.* Stephenson: J. Am Ceram. Soc, **10**, 924 (1927).
[92] Brit. Pat. 342,469 (1928).

a mold the shape of a rubber glove is dipped into the mixture which has been liquefied by stirring; it is then pulled out at such a rate that the mass has solidified when the form has just left the dip. The rubber mixture covers the form in a uniformly thick layer without any suspending drops. After the dipping process, the latex is dried and vulcanized. The problem of mixing large charges equally has retarded the technical application of the procedure.

Drilling Fluids. The application of thixotropic behavior on a large scale is found in the so-called "drilling fluids" used in drilling for petroleum.[93] In this operation the drill passes through layers of clay, quartz, etc. If the boring fluid is water alone, the mixture in the hole will be a concentrated suspension of clay, etc., which may easily settle down for one reason or another and "freeze" the drill. This may be prevented by using as a boring fluid a thixotropic suspension of bentonite which sets, at the worst, to a soft gel which is easily liquefied again.

One of the important functions of a drilling fluid is to seal off gas formations by the hydrostatic head of the fluid column. For this purpose weighted drilling fluids are employed which not only furnish a pressure exceeding that of the gas but will penetrate the formation to a slight extent, thus preventing entrance of gas by diffusion or solution. Ambrose and Loomis calculate that, if the gas pressure is 1500 lb./sq. in. at 2750 ft., the drilling fluid weight per gallon must be at least 10.46 lb./gal. and should be at least 2 lb./gal. heavier to furnish a reasonable excess pressure. Clay suspensions of this density are entirely too viscous for pumping; hence a suitable drilling fluid is made by adding 2–3% of bentonite to mixtures of substances such as barium sulfate and hematite whose suspensions alone have a low viscosity. "Baroid" is a technical mixture of this kind. Just as with latex, the thixotropic bentonite tends to impart thixotropy to the whole mass. The effect of pH on the stability of such suspensions as "Baroid" has been worked out by Ambrose and Loomis and applied to actual drilling practice.

The foreman may test the thixotropic properties of a drilling fluid just as was done with the rubber glove, above mentioned. The hand is dipped into the well-stirred liquid and drawn out slowly, observing whether the solidified mass covers the fingers uniformly without any drops hanging down.

[93] Lawton, Ambrose, and Loomis: Physics, **2**, 365; **3**, 185 (1932); Ambrose and Loomis: **4**, 265 (1933); Ind. Eng Chem, **25**, 1019 (1933).

CHAPTER XXI

BASE EXCHANGE IN SILICATE GELS

Gazzari[1] in 1819 made the interesting and important observation that clay decolorizes liquid manure and retains soluble substances which are given up subsequently to growing plants. This was perhaps the first work on base exchange or exchange adsorption, but it remained for Way[2] in 1850 to elucidate the significance of Gazzari's observation. Way originated the instructive experiment of allowing potassium chloride to percolate through a column of soil which was found to take up potassium but not chlorine and to liberate another element, chiefly calcium, in place of the adsorbed potassium. Similarly Way found that ammonium was taken up by the soil in exchange with calcium. Thus the ingredients, potassium and ammonium, which are indispensable for plant growth are retained in the soil and prevented from leaching, at the expense of the common element calcium. Later, Eichorn[3] showed that among the natural hydrated double silicates several bases are mutually interchangeable. Such substances are now called zeolites. An important example of this class of substances is the synthetic permutite (from *permutare,* to change) first prepared by Gans[4] by fusing 3 parts of kaolin, 6 of sand, and 12 of sodium carbonate, followed by leaching the vitreous mass with water. Gans' preparation is a highly porous, almost amorphous gel which corresponds approximately to the formula $Na_2O \cdot Al_2O_3 \cdot 2SiO_2 \cdot xH_2O$; it may be similar in constitution to the naturally occurring crystalline zeolite of the same composition.

Base-exchange Phenomena

Permutites

If water containing calcium or magnesium chloride is allowed to percolate through a column of sodium permutite, there results a solu-

[1] *Cf.* Sistini: Landw. Vers.-Stat., **16**, 409, 411 (1873).

[2] J. Roy. Agr. Soc Engl., **11**, 313 (1850).

[3] Pogg. Ann., **105**, 126 (1858).

[4] Jahrbuch Kgl. Preuss. Geol. Landesanstalt., **26**, 179 (1905); **27**, 63 (1906); *cf.* Riedel: Ger. Pat. 186,630 (1906); 200,931 (1907); Gans-Riedel: U. S. Pat. 914,405 (1908).

tion of sodium chloride free from calcium or magnesium, and calcium or magnesium permutite is formed. The original permutite is restored by percolating a concentrated solution of sodium chloride through the alkaline-earth permutite, whereby the calcium or magnesium is replaced by sodium. This base exchange is the basis of the permutite process for softening hard water. If sodium or calcium permutite is treated with a solution of a manganese salt, a manganese permutite is produced; and if a solution of potassium permanganate is employed, a potassium-manganese permutite results, covered with a finely divided layer of a higher oxide of manganese. This product is employed to remove iron from water as well as for oxidizing organic matter and bacteria in water. Regeneration is accomplished by treatment with a solution of potassium permanganate.

In many cases, the exchange of cations takes place almost quantitatively. Thus a sodium permutite in contact with a moderately concentrated silver nitrate solution was found by Günther-Schulze [5] to have exchanged 96.5% of its sodium for silver in a day's time. The extent and rate of the exchange depend in large measure on the physical character of the permutite; a freshly prepared sample exchanges bases more completely and quickly than a dried one.[6] Permutites containing but one base can be prepared by leaching the ordinary samples for several months with solutions of the chloride of the metal desired. Hydrogen permutite is prepared by electrodialysis of the ordinary product as described on page 405.

A special siliceous gel known as "doucil" is made [7] by mixing solutions of sodium silicate and sodium aluminate, drying, and washing to remove soluble sodium salts. The dried gel has the approximate composition $Na_2O\ Al_2O_3 \cdot 5SiO_2$ corresponding to the natural crystalline zeolite, phillipsite. Like the zeolites and the artificial permutites, doucil may be employed to soften water and to recover either alkali or alkaline-earth metals from dilute solutions.[8] Unlike most base-exchange silicates, doucil has a very minute gel structure possessing pores of ultramicroscopic dimensions. It therefore exhibits a relatively high exchange capacity for a given mass. "Its high capacity and quick regeneration fits it especially for small domestic softening units although

[5] Z physik Chem., **89**, 168 (1915); *cf.* Bacon: J. Phys. Chem., **40**, 747 (1936).

[6] Beutell and Blaschke: Centr. Mineral. Geol., 142 (1915).

[7] Wheaton· Brit. Pat 177,746 (1922); U. S. Pat. 1,586,764 (1926).

[8] Vail: Trans. Am. Inst. Chem. Engrs., **16** (2), 119 (1924).

it has given excellent results in large industrial units especially designed to take advantage of its properties." [9]

Among the numerous observations on the base-exchange phenomenon in permutites special attention is called to the work of Wieg-

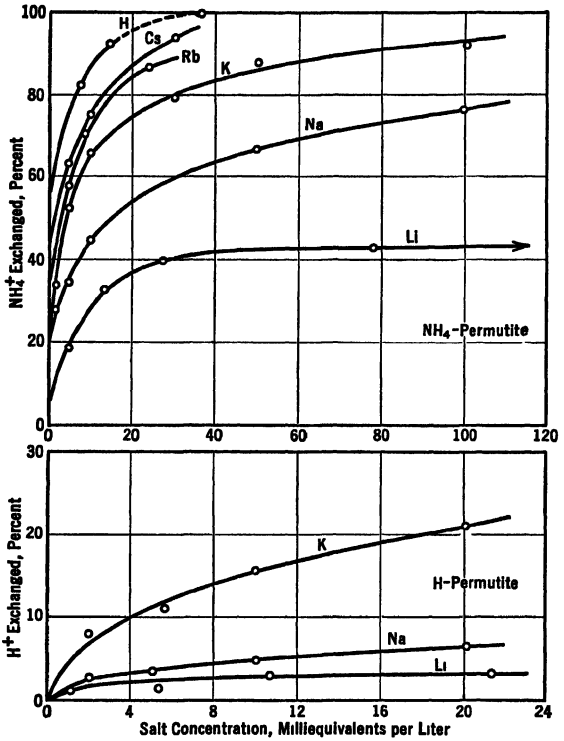


FIG 62.—Isotherms for base exchange with ammonium-permutite and hydrogen-permutite.

ner [10] and Jenny.[11, 12] Some typical data of Jenny are shown graphically in Fig. 62 for an NH_4-permutite and a H-permutite. The ab-

[9] Vail: J. Soc. Chem. Ind., **44**, 214*T* (1925).

[10] J. Landw., **60**, 111, 197, 223 (1912); Kolloid-Z (Zsigmondy Festschrift), **36**, 341 (1925).

[11] Jenny and Wiegner: Kolloid-Beihefte, **23**, 428 (1926); Kolloid-Z., **42**, 268 (1927).

[12] Jenny: Mo. Agr. Expt. Sta. Research Bull. 162 (1931); J. Phys. Chem., **36**, 2217 (1932).

scissas represent the percentage displacement of ammonium and hydrogen respectively, and the ordinates, the equilibrium concentration of the several electrolytes in milliequivalents per liter.

From these and similar data with other permutites and salts, it appears that the capacity of the ions to enter a gel and displace ammonium (or hydrogen) is: $Li < Na < K < Rb < Cs < H$ and $Mg < Ca < Sr < Ba$. Similarly, the ease of replacement of the several ions from alkali permutites by ammonium is: $Li > Na > K > Rb > Cs$. The more highly hydrated ions like Li^+ and Na^+ are prevented by their water envelope from coming as close to the oxygen atoms of the permutite particle as the less hydrated ions. The electric charge is the same for ions of the same valence, but the force of attraction is inversely proportional to the square of the distance between charges; hence the large and voluminous lithium and sodium ions have the lowest displacing power for ammonium and are the most easily displaced by ammonium.

Hydrophilic colloids retard the base-exchange process[13] in the order: gelatin > gum arabic > Irish moss > soil colloids > dextrin > humic acid. The retarding action results chiefly from mechanical effects such as blocking of the pores of the zeolite.

Clay

The exchangeable bases in the soil are found chiefly in the colloidal or clay fraction. This may be extracted from the soil by a suitable method (p. 401) and subjected directly to base-exchange studies. Since a clay may contain various exchangeable cations it is better to work with a pure basic clay which may be prepared by adding the proper amount of the hydroxides of sodium, potassium, ammonium, etc., to H-clay formed by electrodialysis (for details see p. 405).

To illustrate the base exchange in clays, some results of Jenny[14, 15] for an NH_4-Putnam clay and a H-Putnam clay are shown in Fig. 63. From these and similar experiments the adsorption (intake) of univalent cations for Putnam clay was found to be: $Li = Na < K < H$; and for bentonite clay $Na \leqq Li \leqq K < H$; the displacement of the adsorbed ions takes place in the reverse order.

Although a comparison of the exchange adsorption curves for clays and permutites would indicate an analogous behavior, the two classes

[13] Sauer and Ruppert: Kolloid-Z., **78**, 71 (1937).
[14] J. Phys. Chem, **36**, 2217 (1932).
[15] *Cf.* Marshall and Gupta: J. Soc. Chem. Ind., **52**, 433*T* (1933).

of substances are really quite different in certain respects: The permutites are feebly crystalline or amorphous, and have a loose structure from which practically all their cations may be readily replaced by neutral salt solutions; the clays are definitely crystalline, the structure is less porous, and only a part of the bases present are readily replaced

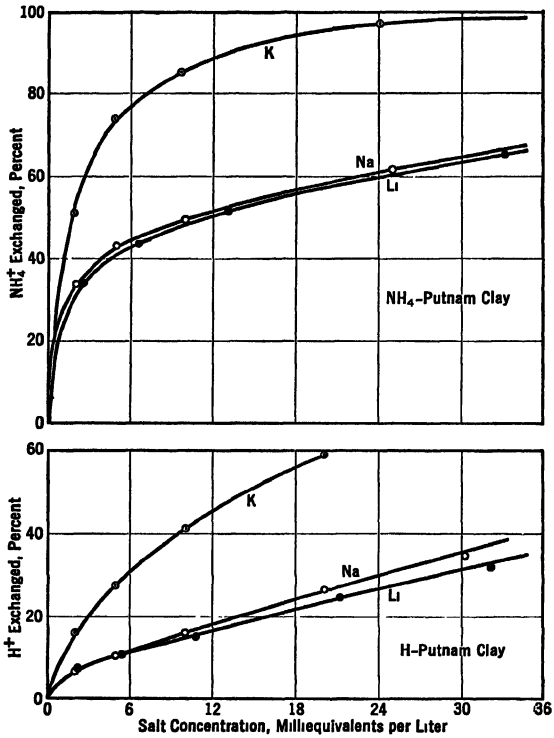


FIG. 63.—Isotherms for base exchange with ammonium-Putnam clay and hydrogen-Putnam clay.

by salt solutions. The maximum exchange capacity of a permutite may be as high as 400–500 milliequivalents per 100 g (m.eq./100 g) depending on the method of preparation, whereas for unground soil colloids and bentonite it is seldom more than 100 m.eq./100 g and usually much less. The base-exchange capacity of permutites is altered but little by grinding whereas that of the soil colloids may be increased

greatly by reducing the size of the individual particles.[16] To illustrate, in Table XLIX are summarized some observations of the effect of grinding in a ball mill on the base-exchange capacity of (1) the zeolite, natrolite; (2) a permutite; (3) bentonites; and (4) soil colloids. Samples under (3) and (4) were calcium saturated, before grinding, by

TABLE XLIX

EFFECT OF GRINDING ON BASE-EXCHANGE CAPACITY

Material	Before grinding		After grinding	
	Particle size	M.eq./100 g	Time, hr.	M.eq./100 g
Natrolite			48	74 5
			72	108 5
Permutite		225 0	48	225 0
Bentonite	1μ	126 0	72	238 0
Beidellite	1μ	50 0	48	200 5
Yolo Soil Colloid	1μ	67 0	48	166 0
Cecil Soil Colloid	1μ	17 0	48	151 0
Redding Soil Colloid	1μ	35 0	48	122 5

leaching with calcium acetate solution. The base exchange is expressed in m.eq./100 g.

Since grinding increases the base-exchange capacity, it might appear that the distinction between exchangeable and non-exchangeable ions in the soil colloids is only apparent and depends on the accessibility of the ions as determined by the state of subdivision of the particles. Actually, both the accessibility and the strength and nature of the attractive force by which the ion is held to the crystal lattice play a rôle. Kelley[17] found by x-ray analysis that grinding may actually destroy the crystal lattice to a certain extent. Kelley's and Jenny's work indicates that all the potassium and sodium and possibly all the calcium in various classes of silicates are replaceable, provided that the particles are made sufficiently small to allow access to these ions.[18] The situation with magnesium, however, is more complex: the octahedral magnesium[19] is probably not replaceable stoichiometrically by alkali and

[16] Kelley, Dore, and Brown: Soil Sci., **31**, 25 (1931); Kelley and Jenny: **41**, 367 (1936).

[17] Trans. Intern. Congr. Soil Sci., 3rd Congr., Oxford, **3**, 88 (1935)

[18] *Cf.* van der Meulen: Rec. trav. chim., **54**, 107 (1935).

[19] Pauling: Proc. Natl. Acad. Sci. U. S., **16**, 123 (1930).

ammonium, especially when OH^- ions are a part of the octahedra. On the other hand, magnesium can replace other replaceable cations reversibly

The loss of ammonia from ammonium permutite, bentonite, and clay increases linearly with the temperature.[20] The loss is practically complete at 300° for the permutite; 450° for the bentonite; and 500° for the clay.

Mechanism of the Base-exchange Process

The pioneer work of Way on base exchange led him to believe that the process was essentially chemical in nature although he recognized certain abnormal characteristics, such as the speed of exchange, influence of temperature, and existence of the lyotropic series, which are not readily accounted for on a purely chemical basis. Liebig [21] took the position that the phenomenon was essentially physical in character, thus starting a controversy that has not yet been settled to the satisfaction of everybody. It is known that the magnitude of the exchange depends on the concentration of the salt solution used in the leaching. A part of the controversy concerning the nature of the base-exchange process has been precipitated by the use of solutions of only moderate concentration, omitting very dilute or highly concentrated systems. Some of the attempts that have been made to express the experimental results mathematically are described in the following paragraphs.

Equations Based on the Law of Mass Action

Gans [4] observed the similarity between base-exchange equilibria and those governed by the mass law and developed the following equation based on the latter, for ions of the same valence:

$$K = \frac{X_2}{(m \cdot n - x)(g - x)}$$

where K is the equilibrium constant; m, the amount of the exchange complex in grams; n, the total amount in mols of exchangeable bases in the complex; g, the total amount of the displacing ion in solution; and x, the amount taken up.

By making use of different assumptions, other mass-action equa-

[20] Bottini: Kolloid-Z., **78**, 68 (1937).
[21] Ann., **94**, 373 (1855).

tions have been set up by Anderegg and Lutz,[22] Kerr,[23] and Vanselow.[24] Marshall and Gupta [25] showed that the various formulations are inadequate to represent the experimental data. Kielland [26] has interpreted some of Marshall and Gupta's data in terms of the mass law by taking into account the so-called activity coefficients of the zeolite components.[27] This mathematical analysis of the data for exchange reactions with H- and Tl-Putnam clay and with H- and Tl-bentonite led to the conclusion that with both materials a definite intermediate compound is formed of the composition $2HZ \cdot TlZ$ where Z stands for the anion portion of the substance. The improbability of the formation of a definite double salt with any clay, and of the same double salt with a Putnam clay and a bentonite, renders Kielland's analysis of questionable value.

Rothmund and Kornfeld [28] point out that Gans' equation is a special case of the more general mass-law equation:

$$\frac{c_1}{c_2} = k\frac{C_1}{C_2}$$

where c_1 and c_2 are the concentrations of the two ions in the solid phase and C_1 and C_2 are the concentrations of the corresponding ions in the liquid phase. According to this equation, which applies through a limited range, the equilibrium is independent of the volume and therefore remains unchanged whether liquid be added or removed. The general relationship between the amount taken up and the equilibrium concentration of the solution is given more nearly by the empirical expression:

$$\frac{c_1}{c_2} = k\left(\frac{C_1}{C_2}\right)^{1/n}$$

where c and C have the same significance as above, and k and n are constants. This equation corresponds to that for the adsorption isotherm. Moreover, the value of the exponent lies between 0.3 and 0.7, as in many typical cases of adsorption.

[22] Soil Sci., **24**, 403 (1927).
[23] J. Am. Soc. Agron., **20**, 309 (1928).
[24] Soil Sci., **33**, 95 (1932).
[25] J. Soc Chem. Ind., **52**, 433*T* (1933).
[26] Tids Kjemi Bergvesen, **15**, 74 (1935); J Soc. Chem Ind, **54**, 232*T* (1935).
[27] *Cf.* Randall and Cann: Chem. Rev., **7**, 369 (1930); Møller: Kolloid-Beihefte, **46**, 1 (1937).
[28] Z. anorg. Chem., **103**, 129 (1918); **108**, 215 (1919); *cf.* Ramann and Spengel: **95**, 115 (1916); **105**, 81 (1918); Ramann and Junk: **114**, 90 (1920).

Equations Based on Adsorption

The similarity in the form of base-exchange and ordinary adsorption curves led Wiegner [29] to conclude that the process is an exchange adsorption. In support of this he found that the exchange process is fairly accurately described by Freundlich's familiar equation $x/m = k\,c^{1/n}$, where x/m is the amount adsorbed per gram of adsorbent; c is the equilibrium concentration; and k and n are constants. Later Jenny [11] modified the equation as follows:

$$\frac{x}{m} = k\left(\frac{c}{a - c}\right)^{1/n}$$

to take care of the fact that the ionic exchange is independent of the dilution (*cf.* p. 122). In the modified equation a represents the original concentration of the added salt.

This empirical expression applied by Jenny to both permutites [11] and clays [14] was found to be quite satisfactory especially in dilute to moderate concentrations with ions of low atomic weight. In a series of experiments with different amounts of electrolyte, the constancy of k is generally much better than $1/n$ which often shows a regular change with concentration. With a given clay and various cations, the values of k are closely related to the hydration of the cations and the mean value of $1/n$ is controlled chiefly by the valences of the two cations involved in the exchange.

Since the exchange reaches a maximum value at sufficiently high concentrations of electrolyte, the parabolic equation of Freundlich will not apply at the higher concentrations. To meet this difficulty, Vageler proposed the equation:

$$y = \frac{x \cdot S}{x + C}$$

where y is the amount taken up per gram of substance; x, the equivalents of salt added per gram of adsorbent; S, the maximum exchange capacity (saturation capacity); and C, the half value, that is, the concentration x at which 50% of S is exchanged. This hyperbolic equation, which is identical in form with the adsorption equation of Langmuir (Vol. I, p. 198), is more satisfactory than the Wiegner equation at high concentrations.[25,30] Over a considerable range it represents the

[29] J. Landw., **60**, 111, 197 (1912); Kolloid-Z. (Zsigmondy Festschrift), **36**, 341 (1929); *cf.* Rabinerson: **62**, 157 (1933).

[30] Kottgen: Z. Pflanzenernähr. Dungung Bodenk., **32**, 320 (1933).

data more accurately provided the soil-water ratio is maintained constant during the experiments.[31]

Pauli [32] has given proof that the application of the law of mass action to colloidal electrolytes leads to an equation corresponding to Langmuir's adsorption equation. To arrive at this simple expression, the surface is regarded as being in equilibrium with one kind of cation only and the assumption is made that all ions which can dissociate from the surface have equal chances of doing so. Neither of these conditions is fulfilled in base-exchange processes—hence the limited applicability of the Vageler-Langmuir equation.

Jenny [33] has set up a simple base-exchange model and, on the basis of kinetic concepts, has formulated an equation by the aid of statistical methods. He considers a planar surface which contains a definite number of attraction spots per unit area. If the ions, atoms, or molecules which are initially adsorbed are designated by b and those which are added to function as exchanging particles by w, then, at equilibrium, the number of cations w adsorbed or released is given by the expression:

$$w = \frac{+ (s + N) \pm \sqrt{(s + N)^2 - 4sN(1 - V_w/V_b)}}{2(1 - V_w/V_b)}$$

where N is the amount of electrolyte (number of ions) added initially; s, the saturation capacity; and V_w and V_b, the volumes of the oscillating spaces of the adsorbed ions.

The applicability of Jenny's adsorption equation is illustrated by some data shown graphically in Figs. 64 and 65 obtained with a purified Putnam clay. In the experiments, 7.5 g of the clay containing 4.50 m.eq. of adsorbed ions were treated with various amounts of the several chlorides in a total volume of 500 cc, and the number of cations in the supernatant solution was determined. The exchange values expressed in terms of saturation capacities (4.50 = 100%) are plotted as abscissas against the electrolyte expressed in terms of S, the saturation capacity (*e.g.*, $4S = 4 \times 4.50$ m.eq.). The lines were calculated with the aid of Jenny's equation, and the observed values are shown as dots, circles, etc. It is apparent that the kinetic equation describes quite well the position and trend of the curves over a considerable concentration range. The agreement between theory and experiment is almost perfect in some instances, but in others systematic deviations

[31] Greene: Trans. Intern. Congr. Soil Sci., 3rd Congr, Oxford, **1**, 63 (1935).
[32] Pauli-Valko: "Elektrochemie der Kolloide," 108 (1929).
[33] J. Phys. Chem, **40**, 501 (1936).

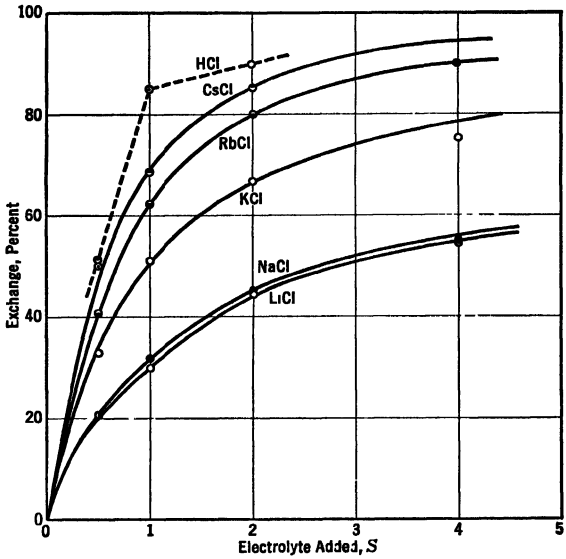


FIG 64.—Exchange isotherms for ammonium-Putnam clay and various univalent cations.

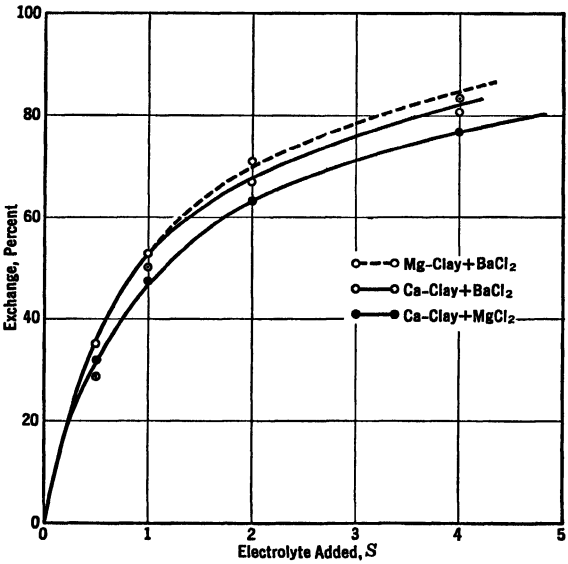


FIG 65.—Exchange isotherms for magnesium-Putnam clay and barium chloride and for calcium-Putnam clay and magnesium and barium chlorides.

seem to occur. The deviations are explained on the basis of structural peculiarities of the colloidal particles and of extreme variations in the properties of the participating ions. Jenny's adsorption equation has the advantage over others in being a developed rather than an empirical expression.

In the light of the above survey it would seem that the base-exchange process should be considered as an exchange adsorption phenomenon rather than as a solid solution phenomenon governed by the mass law. From base-exchange studies with glauconite, Austerweil [34] concluded that the distribution of ions between the zeolite and the solution takes place in accordance with the distribution law or law of extraction, the solid taking the part of a non-miscible liquid. A correlation was found between the extraction formula and Freundlich's adsorption equation.

Application of the Base-exchange Process

The phenomenon of base exchange was first observed in connection with the fixation of fertilizer material by soils, and this is still its most important application. A direct consequence of investigations with clays was the invention of the zeolite or permutite process of water softening to which reference has already been made. Similarly, a knowledge of the principles of base exchange has contributed to the development of modern sugar-refining methods, and one may expect the further application of these principles in such industrial processes as the stabilization of technical emulsions and sols, the tanning of leather, and the manufacture of milk products.

It is now becoming quite generally recognized that base exchange plays an important rôle in the weathering of aluminum silicates which results in the formation of soil The first step in this process appears to be an ionic exchange in which the hydrogen ions of water and carbonic acid replace cations on the surface of the silicate minerals. It is known that clays with the same $SiO_2 : Al_2O_3$ ratio may vary widely in properties because of differences in the nature of the exchangeable cations which are present. Indeed, Gedroiz [35] has proposed a scheme of soil classification based on the nature of the ions adsorbed on the clay particles.[36] The investigations of Gedroiz,[35] de'Sigmond,[37] Kel-

[34] Bull. soc. chim, (4) **51**, 729 (1932); (5) **3**, 1782 (1936).

[35] Kolloid-Beihefte, **29**, 149 (1929).

[36] *Cf.* Bradfield: Trans. Intern. Congr. Soil Sci., 3rd Congr., Oxford, **2**, 134 (1935)

[37] Soil Sci., **21**, 455 (1926).

ley,[38] Burgess,[39] and others on sodium clays have shown that the poor physical condition of alkali soils is caused by, or associated with, a high content of exchangeable sodium and a relatively low salt content. The reclamation of such soils involves the replacing of sodium by calcium ions on an enormous scale (*cf.* p. 412).

The physical as well as the chemical properties of clays may be determined in large measure by the nature of the exchangeable ions. We have seen how the water content of clays will be influenced by the hydration of the exchangeable cations; in the next chapter attention will be called to the rôle played by the exchangeable ions in the phenomena of plasticity, flocculation, and deflocculation of colloidal clays.

[38] J. Am. Soc. Agron, **22**, 977 (1930).

[39] Burgess and McGeorge: Ariz. Agr. Expt. Sta. Tech. Bull., **15**, 359 (1927)

CHAPTER XXII

THE INORGANIC SOIL COLLOIDS

Schlösing[1] in 1874 prepared aqueous suspensions of clay soils which were allowed to stand undisturbed for long periods. In the course of time several distinct layers settled out leaving a sol which contained particles so small that they were invisible in the highest-powered microscope. By this method it was demonstrated that soils contain more or less material in the colloidal state of subdivision.

The inorganic colloidal material in the soil is generally called clay. The International Society of Soil Science in 1913 accepted the following classification of soil particles on the basis of diameters of particles expressed in millimeters: gravel, 20–2; coarse sand, 2–0.2; very fine sand, 0.2–0.02; silt, 0.02–0.002; clay, < 0.002. Colloidal clay is that fraction of the clay whose particles have an effective diameter less than 100 mμ (0.0001 mm). No lower limit is set on the diameter of the clay particle, but experimental evidence places it as low as 10–20 mμ.[2]

Composition of Colloidal Clay

Colloidal Content of Soils

It is difficult, if not impossible, to separate all the colloidal matter from a soil. The earlier investigators merely rubbed up the soil with a considerable amount of water and estimated as colloidal matter the amount that remained suspended for a given length of time. Schlösing[1] was of the opinion that the material which remains longest in suspension differs essentially from material which does not remain suspended so long and so estimated the colloid content of soils to be only 0.5 to 1.5%.[3] Ehrenberg and Given[4] arrived at a similar conclusion. Hil-

[1] Compt. rend, **70**, 1345 (1870); **78**, 1276; **79**, 376, 473 (1874).

[2] Bradfield: J. Phys Chem., **35**, 360 (1931); Colloid Symposium Monograph, **8**, 360 (1931).

[3] *Cf.* Ehrenberg: "Die Bodenkolloide," Dresden, 99 (1922).

[4] Kolloid-Z, **17**, 33 (1915).

gard [5] and Williams [6] reported much higher percentages based on the amount of material that does not settle in a 24-hour period.

Since the amount of soil that will remain suspended depends on the degree of peptization of a gel and the time of settling, methods of estimating the colloid content of soils based on such procedures [7] are necessarily inaccurate. Other methods that have been employed are based on determination of the adsorption capacity of the soil for malachite green,[8] water, and ammonia. Gile [9] and his coworkers determined the adsorption capacity of a sample of soil and of the colloidal material extracted from the soil, and from these data calculated the percentage colloidal matter. After correcting for the possible alteration in adsorptive capacity of the colloid produced by extraction, the percentages of colloidal matter indicated by adsorption of malachite green, water, and ammonia showed fairly good agreement among themselves [10] and with the percentages estimated gravimetrically and microscopically. Bouyoucos [11] estimated rapidly the colloidal material in a soil suspension by means of a specially made hydrometer. As would be expected, the colloidal content of different soils varied widely. Assuming that all particles less than 1 μ in diameter are colloidal, the sandy soils contain but a few per cent of colloids, whereas the loam soils may contain 15–25%, and the clayey soils 40 to 50 and up to 90% colloidal matter.

Extraction of the Colloidal Fraction

The separation in quantity of the colloidal fraction of soils was made possible by the development of continuous-flow centrifuges capable of developing a centrifugal force of 40,000 times gravity. The method of procedure developed independently by Moore, Fry, and Middleton [12] in the Bureau of Soils of the U. S. Department of Agriculture and by Bradfield [13] is essentially as follows.[14] The soil, prefer-

[5] Am. J Sci, (3) **6**, 288, 333 (1873); "Soils," New York, 333 (1919)

[6] Forschr Gebiete Agrikultur-Physik, **18**, 225 (1895).

[7] Scales and Marsh. Ind. Eng. Chem, **14**, 52 (1922).

[8] Ashley U S. Geol Survey, Bull, **388**, 65 (1909).

[9] Gile, Middleton, Robinson, Fry, and Anderson: U. S. Dept. Agr. Bull. 1193 (1924).

[10] *Cf* Davis. J. Am. Soc Agron., **17**, 277 (1925).

[11] Soil Sci., **23**, 319 (1927), **25**, 365, 473; **26**, 233 (1928); *cf*, *however*, Slegel: J. Am. Ceram. Soc., **11**, 185 (1928).

[12] Ind Eng. Chem., **13**, 527 (1921).

[13] Mo Agr. Expt. Sta. Research Bull. 60 (1923).

[14] Bradfield· Alexander's "Colloid Chemistry," **3**, 569 (1931).

ably fresh from the field, is agitated vigorously with 3 to 5 times its weight of water for several hours and allowed to settle from 1 to 10 days. The suspended material is then siphoned off and passed through the centrifuge at a rate sufficient to deposit all the non-colloidal material in the bowl. The colloidal fraction is concentrated by passing through the centrifuge at a slower rate [14] or by the aid of a Pasteur-Chamberlain filter. Under favorable conditions the sol prepared in this way is stable almost indefinitely. The colloidal matter dries in the air to a hard, brittle mass which consists of secondary aggregates that may be as difficult to disperse as the original sol. The binding power of the clay when mixed with sand, molded into briquettes under high pressure, and dried, is greater than that of Portland cement.

Analysis of the Colloidal Fraction

Before Electrodialysis. The chemical composition of the colloidal fraction of soils seems to depend more on the environment under which it is found than on the nature of the parent material. This is illustrated by Table L which gives Bradfield's [14] analyses of the col-

TABLE L

CHEMICAL COMPOSITION OF COLLOIDAL CLAY

	Memphis	Robertsville	Boone D	Boone C	Clarksville	Wabash	Sharkey	Bates	Putnam B P	Marion	Cherokee	Average
H_2O 105° C	10 60	10 86	11 28	12 30	12 66	12 58	12 83	12 46	12 17	12 44	10 69	11 90
Volatile matter	11 76	13 38	12 47	11 88	11 34	11 16	11 51	12 43	13 37	11 83	14 09	12 29
SiO_2	50 00	49 81	48 77	50 54	51 34	50 11	52 78	51 18	50 22	52 15	48 79	50 11
Al_2O_3	28 21	29 23	29 90	28 86	28 00	24 51	24 19	25 59	27 65	26 53	30 42	27 55
Fe_2O_3	3 53	3 72	4 05	4 45	4 53	3 39	4 73	5 17	4 74	5 51	3 80	4 33
CaO	1 14	0 94	0 23	0 73	0 29	1 75	1 23	0 99	0 92	0 44	0 35	0 82
MgO	1 84	1 51	1 37	1 42	1 54	2 41	2 56	1 80	1 52	1 75	1 29	1 73
K_2O	1 68	1 25	0 80	1 01	1 25	1 87	1 63	1 34	0 85	1 06	1 03	1 25
Na_2O	0 600	0 000	0 120	0 071	0 301	0 602	0 854	0 318	0 449	0 302	0 555	0 379
MnO_2	0 056	0 018	0 007	0 028	0 021	0 027	0 023	0 025	0 014	0 018	0 017	0 023

loidal clay extracted from Missouri soils of diversified types with respect to origin, topography, age, and source of parent material. These clays show great uniformity in their content of SiO_2, Al_2O_3, Fe_2O_3, and combined water. In contrast, Robinson and Holmes,[15] who analyzed the colloidal fraction from 45 different soils from various parts

[15] U. S. Dept. of Agr. Bull. 1311 (1924).

of the United States, observed a much wider variation in composition as follows: SiO_2, 31.84 to 55.44%; Al_2O_3, 16.42 to 38.28%; Fe_2O_3, 4.66 to 16.67%; and combined water, 3.33 to 16.56%.

After Electrodialysis. Reference to Table L discloses that various amounts of alkali and alkaline-earth metals are present in the colloidal clays, the total amount on the average for these clays being almost one equivalent for every molecule of ammonia. In the presence of water the finely divided clay hydrolyzes to a certain extent, hydrogen ions from water replacing the alkali or alkaline-earth cations. Under natural conditions, this process is favored by the presence of carbonic acid. In the laboratory, the replacement process can be accomplished

TABLE LI

ANALYSES OF ELECTRODIALYZED COLLOIDAL MATERIAL FROM A SERIES OF CLAYS

	Putnam	Putnam + H_2O_2	Susque-hanna	Boone	Sharkey	Rock River Ben-tonite	Chey-enne Ben-tonite	Finest Chey-enne Ben-tonite
Loss on ignition	17.75	17 60	19 35	17 78	17 31	16 36	17 97	18 94
SiO_2	47 84	47 86	45 66	45 73	50 58	57 01	57 15	56 25
Al_2O_3	23 75	23 11	22 68	23 57	20 21	20 58	18 37	19 03
Fe_2O_3	7 62	8 25	8 14	9 90	6 98	3 61	3 00	2 97
FeO	0 29	0 08	0 31	0 23	0 31	0 09	0 09	0 12
MnO	0 02	. .	0 01	0 02	0 03	0 01	0 00	0 00
TiO_2	0 52	0 52	1 02	0 48	0 54	0 12	0 29	0 22
CaO	0 11	0 08	0.10	0 08	0 10	0 11	0 14	0 08
MgO	1 49	1 22	1 95	1 14	2 03	1 94	2 86	2 59
K_2O	1 16	1 20	0 70	0 72	1 44	0 02	0 02	0 02
Na_2O	0 07	0 05	0 05	0 10	0 11	0 02	0 00	0 02
C	0 977	0 184	0 667	0 566	0 591	0 055	0 198	0 073
P	0 04	0 13	0 07	Trace	Trace	Trace	Trace	Trace
S	0 014	0 010	0 014	0 015	0 025	0 019	0 005	0 011
Sum *	100 67	100 11	100 05	99 77	99 67	99 89	99 90	100 25
SiO_2/Al_2O_3	3 42	3 52	3 41	3 28	4 24	5 30	5 28	5 01
†	104 9	91 0	117 6	78 4	139 3	102 0	148 4	133 4
‡	70	75.	80	70	80	90	100	110
§	40.0	45 2	42 6	47 0	36 5	46 8	40 3	45 0

* Carbon is included in loss on ignition.
† Non-exchangeable bases. Milliequivalents.
‡ Exchangeable cations (approximate). Milliequivalents.
§ [Exchangeable/(exchangeable + non-exchangeable)] × 100.

much more rapidly and completely by electrodialysis [16] which removes the replaced cations continuously. The colloidal clay is placed in the middle section of a three-compartment cell between membranes which are permeable to the ions hydrolyzed off the particles but impermeable to the colloidal clay ions themselves. Distilled water is flowed slowly through the outside compartments in which are suspended suitable electrodes (platinum for anode and nickel for cathode) and a potential of 100–200 volts is applied. The cations appear in the form of their hydroxides in the cathode chamber, and the anions, which are the clay micelles, migrate to the anode membrane and accumulate there; any soluble acid which can pass the membrane is removed.

Only a part of the total bases, usually from 25 to 50%, are removed by electrodialysis. This is shown by Schollenberger's analyses of clays electrodialyzed by Bradfield, Table LI. It will be seen that the calcium and sodium ions are almost completely removed from all samples whereas the potassium and magnesium are more firmly held (*cf.* p. 393). If a clay from which no more base can be removed by electrodialysis is allowed to deposit on the anode membrane, the water in which it was suspended will be neutral whereas the clay paste will have a *p*H value of 2.0 to 3.5.

Constitution of Colloidal Clay

Mineral Constituents

Clays are secondary products formed as a rule by the weathering action of water, carbonic acid, etc., on feldspar and feldspathic minerals. In view of the manner in which the clays are formed and laid down, it is not surprising that they should show considerable variation in composition. The chemical composition being known, the question naturally arises as to the constitution of the clays. Of the several possibilities, the bulk of the evidence supports the view that the colloidal fraction of soils consists of new secondary minerals with which may be mixed small amounts of the separate oxides or the primary minerals. Another theory which used to be regarded with considerable favor assumes that the weathering influences transform the hydrated silicates into the hydrous oxides of iron, aluminum, and silicon together with soluble salts of sodium, potassium, and calcium which are adsorbed in part by the hydrous oxide gels. A third possibility is that the clay consists merely of colloidal fragments of the coarser mineral from which it was derived.

[16] Bradfield: Proc. 1st Intern. Congr. Soil Sci, **2**, 264 (1927).

The strongest evidence against the view that the colloidal fraction of soils consists of mixtures of the hydrous oxides of iron, aluminum, and silicon with adsorbed salts, or of fragments of the parent minerals, is furnished by x-ray diffraction analysis of clays by Wherry, Ross, and Kerr,[17] Hendricks and Fry,[18] Pauling,[19] Kelley, Dore, and Brown,[20] Hofmann, Endell, and Wilm,[21] and others.[22] Although the diffraction patterns are not always as sharp as they should be for precise analysis, they reveal that the bulk of the material in the soil colloids is crystalline, the most common constituents being secondary "clay minerals" of two types as follows: (1) the halloysite type which includes halloysite ($Al_2O_3 \cdot 2SiO_2$ $4H_2O$),[23] metahalloysite,[23] kaolinite,[24] nacrite,[25] and dickite;[26] (2) the prophyllite type which includes prophyllite ($Al_2O_3 \cdot$ - $4SiO_2$ H_2O) and talc, montmorillonite ($MgO \cdot Al_2O_3$ $5SiO_2 \cdot nH_2O$, the major constituent of most bentonites), beidellite ($Al_2O_3 \cdot 3SiO_2 \cdot$ - nH_2O, which gives the same x-ray diffraction pattern as montmorillonite[21]), and nontronite[27] (Fe_2O_3 $3SiO_2$ nH_2O). Notable exceptions are the laterites which contain, in addition to aluminosilicates, hydrous α-$Al_2O_3 \cdot H_2O$ (diaspore) and α-Fe_2O_3 H_2O (göthite); and certain bauxite clays which contain hydrous γ-$Al_2O_3 \cdot H_2O$. The primary soil minerals such as quartz, micas, and feldspars are present only in very small amounts. This indicates strongly that the soil colloids do not result from mere reduction in size of the original mineral with alterations caused by surface weathering, but from a secondary synthesis of the degradation products of the primary minerals.

The absence of the primary minerals in the colloidal state is probably attributable to their instability in the presence of water, carbonic acid, and air. Formed under conditions of high temperature and pres-

[17] Colloid Symposium Monograph, **7**, 191 (1930).

[18] Soil Sci., **29**, 457 (1930)

[19] Proc Natl Acad Sci U. S., **16**, 123, 578 (1930)

[20] Soil Sci., **31**, 25 (1931)

[21] Z angew Chem., **47**, 539 (1934); *cf* Hofmann and Bilke. Kolloid-Z, **77**, 238 (1936)

[22] *Cf* Jacob, Hofmann, Loofmann, and Maegdefrau Beihefte Z Ver deut Chem, **21**, 11 (1935); Trans Intern Congr Soil Sci, 3rd Congr, Oxford, **1**, 88 (1935); Dubrisay and Trillat· Rev. gén. colloïdes, **8**, 1 (1930); *for a summary see* Marshall· Z. Krist, **91**, 433 (1935); J Phys Chem, **41**, 935 (1937).

[23] Mehmel· Z Krist., **90**, 35 (1935).

[24] Gruner: Z Krist, **83**, 75 (1932)

[25] Gruner: Z Krist., **85**, 345 (1933).

[26] Gruner. Z. Krist, **83**, 394 (1932).

[27] Gruner· Am. Mineral, **20**, 475 (1935).

sure,[28] they break down when exposed to weathering agents, forming new compounds which are more stable under the new conditions. The rate at which these processes go on increases so rapidly with decreasing particle size that a particle of colloidal dimensions, below 100 mμ, can exist as a primary mineral for a short time only. Since the rate at which large particles are reduced to colloidal size is slower than the rate at which the colloidal particles of the primary minerals are destroyed, it follows that the modal fraction of the size-frequency curve of the primary minerals will tend to remain well above the colloidal range. On the other hand, the modal fraction of the clay minerals must lie within the colloidal range since they are seldom present in the fine sand or silt fractions.

Further evidence against the hypothesis that colloidal clays are mixtures of hydrous oxides with adsorbed salts is the failure to prepare synthetic clays which possess more than a superficial resemblance to natural clays. To illustrate, the permutites which have base-exchange properties analogous in certain respects to clays and which have been suggested for use as "models," [29] differ from clays in many respects: As we have seen, the clays give an x-ray diffraction pattern whereas the permutites are less highly hydrated and are almost amorphous to x-rays. Moreover, practically all the cations of permutites are replaced at ordinary temperatures by the cations of neutral salt solutions whereas only 30–50% of the cations of clays are readily replaced by treating with neutral salts. Also, an electrodialyzed clay is a much stronger acid with a much greater capacity to absorb bases than an electrodialyzed permutite. Finally, the adaptation of mineralogical methods to the determination of mean refractive index, mean density, and double refraction of particles smaller than 100 mμ,[30] and recent investigations of the base-exchange phenomenon in clays [31] (p. 391), furnish strong confirmatory evidence in support of the view that the colloidal fraction of soils consists essentially of aluminosilicates rather than of varying mixtures of the hydrous oxides.

Water

The water content of soil colloids is either adsorbed water or water of crystallization, that is, contains OH^- ions as a part of a crystal

[28] *Cf* Ewell and Insley: J Research Natl. Bur. Standards, **15**, 173 (1935).

[29] *Cf* Wiegner: J Landw., **60**, 110, 197 (1912).

[30] Marshall. Trans Faraday Soc, **26**, 173 (1930); Z. Krist., **90**, 34 (1935); J. Phys Chem., **41**, 935 (1937).

[31] *Cf., for example,* Kelley and Jenny: Soil Sci., **41**, 367 (1936).

lattice structure. Drying air-dried samples at 110° results in a loss of 8–12% of adsorbed water depending on the vapor pressure and temperature at which they are air dried. This adsorption is almost completely reversible even when the dehydration is accomplished at higher temperatures. Indeed, Kelley, Dore, and Brown [20] found that bentonite clays can be heated to 350° without any appreciable change in their base-exchange capacity or x-ray diffraction pattern; and Kelley, Jenny, and Brown [32] called "adsorbed water" that proportion of the total water which comes off at 400° from such clays, provided that

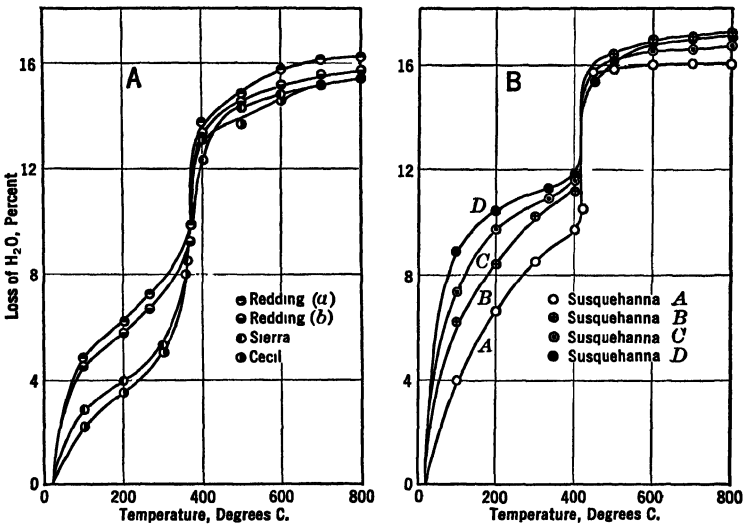


FIG 66.—Dehydration curves for typical soil colloids.

there is no evidence of the loss of crystal water at this temperature Heating from 400 to 700° causes an additional loss of water with a complete and irreversible loss of colloidal properties [33] including base-exchange capacity.[34]

Kelley, Jenny, and Brown compared the dehydration isobars for a number of minerals of known structure with those for typical soil colloids. Some isobars for soil colloids are given in Fig. 66*A* and *B*.

[32] Soil Sci., **41**, 259 (1936).

[33] Brown and Montgomery: Bur. Standards Tech. Paper 21 (1913).

[34] *Cf. the behavior of zeolites,* Milligan and Weiser: J. Phys. Chem., **41**, 1029 (1937).

From such curves the amount of adsorbed and crystal lattice water in several clays is deduced as given in Table LII. Unlike minerals of known structure the soil colloids lose their lattice water at lower temperatures, but it is not certain whether this is caused by particle size alone, or by structural differences, or by both. It seems most likely that both factors come in since the soil colloids are, in general, somewhat different from the pure clay minerals. Thus, of the two major classes of soil colloids the first resemble in some measure kaolinite and

TABLE LII

ADSORBED AND CRYSTAL LATTICE WATER IN SOIL COLLOIDS [32]
(Anhydrous basis)

Soil colloid	Water in per cent		
	Total	Adsorbed	Crystal lattice
Cecil	18 04	4 74	13 30
Sierra	18 19	4 81	13 38
Redding	19 40	8 01	11 39
San Joaquin	14 54	5 41	9 13
Placentia	18 03	5 74	12 29
Yolo	21 83	12 12	9 67
Susquehanna A	19 12	10 61	8 51
Susquehanna B	21 07	14 01	7 06
Susquehanna C (10–20 in.)	20 75	13 39	7 36
Susquehanna D (10 ft.)	21 08	14 12	6 96
Susquehanna E (11 ft.)	29 29	23 61	5 68
Putnam	15 30	7 25	8 05

halloysite and the second appear to be related to but are not identical with beidellite (p. 406). From a comparison of dehydration isobars for the soil colloids and known minerals, Kelley, Jenny, and Brown deduce that the composition of the surfaces of the former is similar in all cases, consisting of Si-O-Si planes and possibly OH planes on which the water is adsorbed.[35] The possibility of some so-called broken-bond adsorption on linked tetrahedra surfaces is not excluded, but such surfaces are largely absent in the soil colloids.

The addition of water to a colloidal clay dried at 105° is accompanied by a considerable heat of adsorption. Bouyoucos [36] proposed

[35] *Cf.* Marshall: J. Phys. Chem., **41**, 935 (1937).
[36] Science, **60**, 320 (1924).

the phenomenon of heat of wetting as a means of estimating the colloidal content of the soil. As would be expected, the colloids of different soils vary widely in their heat of wetting, owing to the difference in their physical character. Heating to 750° is said to decrease the heat of wetting of soils to zero; but this cannot be strictly true, since the adsorptive capacity of ignited soils may be 30 to 50% of the value before ignition. Because of this loss of adsorptive capacity on ignition, Alway [37] questions the reliability of the water-adsorption method of estimating the colloid content of the soil. This seems to be beside the point, since one might reasonably expect the coalescence accompanying ignition to decrease materially the amount of colloidal matter. The validity of the water-adsorption method depends primarily on whether non-colloidal material in unheated soil adsorbs an appreciable amount of water under the conditions of determination.

The total water-holding capacity of a soil is influenced to a considerable extent by the height of the soil column and by the mode of packing of the particles; but the colloidal content is by far the most important factor in determining the moisture-holding capacity. Bouyoucos [38] found that some ordinary clays will hold as much as 75% water as compared to only 20% in some coarse sands.

Not only do the colloidal particles adsorb and conserve water for times of drouth, but the freezing point of water is lowered very appreciably when it is adsorbed.[39] As in the case of the hydrous oxide gels,[40] a part of the adsorbed water is not frozen until the temperature is reduced several degrees below zero. This is doubtless of importance in preventing complete desiccation of the soil by freezing and the consequent destruction of the soil bacteria.

Physical Properties of Colloidal Clay

General Properties

The Silica-Sesquioxide Ratio. In Table LIII [14] are summarized the general properties of a few typical clays investigated by Anderson

[37] Colloid Symposium Monograph, **3**, 241 (1925); Puri, Crowther, and Keen: J. Agr. Sci, **15**, 68 (1925).

[38] Colloid Symposium Monograph, **2**, 132 (1924); *cf.* King: Wis. Agr. Expt. Sta., Sixth Rept., 189 (1889); Alway and McDole: J. Agr. Research, **9**, 27 (1917).

[39] Bouyoucos and McCool: Mich. Agr. Expt. Sta., Tech. Bull., 31 (1916); 36 (1917); Parker: J. Am. Chem. Soc., **43**, 1011 (1921).

[40] Foote and Saxton: J Am. Chem. Soc., **38**, 588 (1916).

TABLE LIII

SUMMARY OF PROPERTIES OF A SERIES OF COLLOIDAL CLAYS

Property	Kind of clay						
	Fallon	Sharkey	Marshall	Susquehanna	Sassafras	Norfolk	Aragon
Molecular ratio—SiO_2/R_2O_3	3 62	3 11	2 73	1 99	1 85	1 60	0 55
Sp gr. in H_2O	2 766	2 718	2 627	2 715	2 748	2 708	..
Av. diam. of particles—$m\mu$	102	91	106	141	128	129	.
Surface M^2/g	21 3	24 2	21 5	15 7	17 0	17 1	. .
No. of particles/g $\times 10^{-12}$	680	960	613	263	335	322	.
Heat of wetting, cal /g	17 5	16 3	14 6	5 3	9 8	7 6	8 0
H_2O absorbed over 30% H_2SO_4 g/g	0 178	0 160	0 130	0 052	0 114	0 084	0 089
Moisture equivalent—%	120	94	72	67	62	62	(Bentonite)
Vol. in H_2O—cc/g	2 5	1 9	1 8	2 0	1 8	1 8	9 0
Relative vis. of 2% sols	1 33	1 14	1 23	1 27	1 33	1 12	
Exchbl Ca+Mg+Na+K, m.eq./g.	1 08	0 69	0 53	0 09	0 23	0 09	
pH	8 2	6 8	7 1	5 6	5 7	5 3	
Organic matter—%	1 79	3 83	7 94	1 86	1 88	2 18	5 96

and Mattson.[41] As a result of numerous observations,[42] it has been found that a number of physical properties of clays may be correlated with the contents of the major constituents as expressed by the ratio of silica to alumina plus ferric oxide. Thus, reference to Table LIII shows a significant correlation between this ratio and the heat of wetting of a series of oven-dried clays. Moreover, swelling, viscosity, dispersibility, heat of wetting, adsorption of bases and basic dyes, and base exchange are all manifested to a greater extent by clays with a high silica-sesquioxide ratio than by those in which this ratio is low.[41,43] Clays with a high ratio are also more electronegative, as indicated by the quantity of aluminum chloride or basic dye solution required to neutralize the negative charge on the particles.[44] The particles with a high proportion of silica and bases remain electronegative in acid as well as in neutral and alkaline solutions, whereas those with a high proportion of sesquioxides are amphoteric and become positive in acid solutions. In accord with this behavior, clays high in sesquioxides

[41] U. S. Dept. Agr., Bull. 1452 (1926).

[42] *Cf.* Anderson: J. Agr. Research, **28**, 927 (1924); Gile, *et al*: U. S. Dept Agr., Bull. 1193; Robinson and Holmes: 1131 (1924); Anderson and Mattson: 1452 (1926); Science, **62**, 114 (1925).

[43] Mattson: J. Am. Soc. Agron., **18**, 458, 510 (1926); Proc 1st Intern. Congr. Soil Sci., **2**, 185 (1927).

[44] Mattson: J. Phys. Chem., **32**, 1532 (1928).

adsorb anions such as chloride and sulfate from acid but not from neutral solutions.[45] Clays with a high proportion of silica give stronger acids when saturated with hydrogen ions.[46]

Although the above-mentioned observations indicate the existence of a relationship between the colloidal behavior of clays and their silica-sesquioxide ratio, it should be emphasized that this is only qualitative and that the physical-chemical constants of a clay cannot be predicted with any degree of accuracy from the observed ratio. This is readily understood when it is recalled that in certain clays all the silica and alumina may be present in an aluminosilicate combination and in others a part may exist as free hydrous alumina or silica having different properties.

The relationship between composition and colloidal properties is well illustrated by the varying behavior of the clay soils of the humid, temperate regions and those of the tropics. A soil of the first type containing 50% or more of clay drains slowly and cannot be plowed without "puddling" for several days after a heavy rain, whereas a red soil of the second type with a similar content of colloidal matter can be plowed within a few hours after a tropical rainstorm. The non-plastic tropical clays are formed under conditions of high temperature and heavy rainfall accompanied by luxuriant plant growth, all of which intensify the weathering processes. This may result in the removal of most of the silica, giving a soil consisting largely of the hydrous sesquioxides of iron and aluminum. Because of their brick-red color such soils have been called laterites.

Exchangeable Cations. In the preceding chapter, brief attention was given to the importance of the nature of the exchangeable cations on the properties of soils (p. 399). The undesirable acid soils of the humid regions possess a low "degree of saturation with bases," and the poor alkali soils of the arid regions possess a high content of exchangeable sodium. Between these two extremes are found the most desirable soils, those which are comparatively rich in exchangeable calcium and usually contain a reserve of calcium carbonate so that they remain largely saturated with calcium.

The saturation capacity of a soil is defined as the sum of the exchangeable bases and exchangeable hydrogen. The acid soils of the humid region have resulted from the gradual displacement of more or less of the desirable calcium by hydrogen, and the alkali soils of the arid regions from the displacement of calcium by sodium. The low

[45] Mattson: Proc. 1st Intern. Congr. Soil Sci, **2**, 199 (1927).

[46] Baver and Scarseth: Soil Sci., **31**, 159 (1931).

productivity of the so-called alkali soils of western United States is undoubtedly connected with the high proportion of exchangeable sodium in the colloid fraction, which renders the clay more highly dispersed, more slowly permeable, and, in extreme cases, almost impermeable to water and air. As Bradfield[47] points out, the removal of soluble salts by leaching with water is not sufficient to restore such soils to productivity; on the contrary, if the soil contains no calcium or magnesium carbonate, such leaching may make conditions worse. To regain the normal physical conditions of such soils, the essential thing is to restore the normal calcium-sodium ratio. If the soil contains a large reserve of calcium carbonate, irrigation with adequate drainage will eventually bring about normal conditions.[48] If calcium must be added, time will be saved by using the more soluble gypsum in place of calcium carbonate. In a soil containing some calcium carbonate, the most economical way to restore the normal calcium-sodium ratio consists in adding sulfur, which is oxidized to sulfate by soil organisms. Acid soils must be treated with lime or calcium carbonate.

Because of the importance of the concept "degree of saturation with bases" for the characterization of soils, many methods have been proposed for determining this value. The results vary with the method of procedure and are not always comparable. This raises the question as to what is meant by a base-saturated soil. Bradfield[49] answers the question in a logical way by defining a soil saturated with bases as one which has reached equilibrium with a surplus of calcium carbonate and the partial pressure of carbon dioxide existing in the atmosphere, and at a temperature of 25°.

In support of the above definition Bradfield showed: (1) that the amount of calcium taken up is independent of the amount of excess added; (2) that the amount adsorbed is the same regardless of the direction or method by which the equilibrium is approached; and (3) that the total amount of base adsorbed is practically independent of the amount and nature of the bases originally present. Moreover, the proposed saturation point represents a natural transition point in physical and chemical properties which are of particular significance in soil science. Thus clays saturated with calcium coagulate in the form of large stable granules which give calcareous soils their well-known improved structure. As soon as excess calcium carbonate is removed the percolating waters charged with carbonic acid bring about a re-

[47] Alexander's "Colloid Chemistry," **3**, 587 (1931)
[48] Kelley and Brown: Soil Sci, **20**, 477 (1925).
[49] Proc. 2nd Intern. Soc. Soil Sci., *A*, 63 (1933).

placement of calcium ions with hydrogen ions, the initial step in soil degradation.

Plasticity

Plasticity is defined as the property of a material which enables it to change its shape without cracking when subjected to pressure, the new shape being retained when the deforming stress is removed. Fine dry sand is not plastic, but it becomes plastic when moist since the solid adsorbs the liquid giving thin films which bind the particles together while still allowing them to move relatively to one another. Moreover, the tendency of liquid surfaces to coalesce causes any break to heal. Hence an adsorbed liquid film may be all that is necessary to render a mass plastic in the ordinary sense.

In the clay industry, the term plasticity connotes not only that the clay can be molded under pressure but also that it will harden under the application of heat, forming a rock-like mass. From this point of view wet sand alone is not plastic but requires the presence of some binding material of a gelatinous character. Rohland [50] considers plastic clay to consist of very minute, non-plastic grains or cores surrounded by gelatinous films of material which are saturated with water when the maximum plasticity is developed. With an excess of water above that for maximum plasticity, the clay becomes "sticky"; and with a still larger excess, a non-plastic sol or clay "slip" is formed. If the clay is dried the gelatinous matter shrinks, becomes hard and horny, and the plasticity disappears only to reappear when the clay is moistened again.

The gelatinous binding material in the colloidal fraction of soils is chiefly hydrous aluminosilicates together with more or less hydrous alumina and silica. Since such substances tend to lose their power of taking up water and re-forming a gel after they have once thoroughly dried out, it is necessary to postulate the presence of something which prevents the gel-forming process from becoming non-reversible. Bancroft and Jenks [51] give experimental evidence to support the view that a gelatinous film can be produced and maintained by the presence together of at least one salt which tends to peptize the clay or some portion of the clay and of at least one salt which tends to coagulate the same portion of the clay.

If one accepts the hypothesis that the gelatinous character of a clay results from aging in the presence of both peptizing and flocculating

[50] Z. anorg. Chem., **31**, 158 (1902).
[51] J. Phys. Chem., **29**, 1215 (1925).

agents, it follows that a non-plastic clay is one which contains but little salts or which has not developed plasticity because of too uniform conditions. The "rotting" of dug clay which increases its plasticity is probably due to the moisture and temperature variations which increase the amount of gelatinous material.

Since a gelatinous body consists of very finely divided particles that have adsorbed water strongly, it follows that a mixture of hydrous oxides or a hydrous aluminum silicate will continue to impart plasticity to a mass, even after drying repeatedly, provided the primary particles are prevented from coalescing or from agglomerating into dense aggregates. As already noted, such coalescence or agglomeration is inhibited by a suitable peptizing agent. One would expect a protecting colloid to exert a similar influence. Since humus doubtless possesses the properties both of a peptizing agent and a protecting colloid, it is probable that it plays an important rôle in the development and maintenance of plasticity in many clays.[52] Ries [53] showed that the addition of a 1% solution of tannin to a clay noticeably increased the plasticity and at the same time deflocculated or peptized the larger aggregates; in addition, the tensile strength of the clay was doubled by this treatment. Acheson [54] increased the plasticity of clays by adding tannin and alkalis until the hydrous mass was completely deflocculated, after which sufficient acid was added to coagulate the colloids to a pasty mass. Everyone knows how Pharaoh increased the burdens of the Israelites by withholding from them the straw which they used in making bricks. It is possible, but not proved, that the straw served as a source of tannin rather than as a binding material and that the burden imposed consisted in their having to make bricks with less plastic material.

Since, from the above point of view, the important thing for plasticity is relatively fine particles coated with a film of colloidal matter which adsorbs water strongly, it should be possible to increase the plasticity by grinding. It is very difficult indeed to grind particles to ultramicroscopic dimensions; nevertheless, the plasticity of certain clays both soft and hard has been increased appreciably by prolonged grinding.[55] Johnson and Blake [56] claim to have made a non-plastic

[52] *Cf.* Keppeler: Chem.-Ztg, **36**, 884 (1912).

[53] Trans. Am. Ceram. Soc., **6**, 44 (1904).

[54] Trans. Am Ceram. Soc., **6**, 31 (1904).

[55] Searle: Brit. Assoc. Advancement Sci., 3rd Rept. on Colloid Chem., 131 (1920); Walker: J. Am. Ceram. Soc, **10**, 449 (1927).

[56] Am. J. Sci., (2) **93**, 351 (1867).

china clay plastic by this means; but they attributed this to the flattening out of the particles rather than to disintegration.

People who do not regard the presence of suitable colloidal matter as a necessary criterion for the plasticity of clays, as the ceramist uses the term, usually attribute the phenomenon to some purely chemical characteristics of the molecules of a clay substance,[57] or to plate-like structure of the particles.[58, 56] The evidence for the existence of a true clay is lacking; but one may be justified in attributing plasticity solely to the plate-like or lamellar structure which the particles possess. Bradfield[59] sees no reason why it is necessary to postulate an extraneous colloidal material to account for the plasticity of clays containing from 40 to 60% colloidal clay which is known to consist of highly hydrated plate-shaped crystals having a variable spacing between certain groups of sheets. Bradfield compares the difficulty of separating two glass plates with a film of water between them with that of two spheres in contact with each other at a single point and with an annular ring of water around the point of contact; and concludes that the plate system if reduced to colloidal dimensions would probably give a much more plastic mass than a system of spheres. Certainly the shape of the particles of colloidal clay would be expected to influence the plasticity of clay, but it is still an open question whether the shape of the hydrated particles is alone sufficient to produce the phenomenon.

Flocculation of Clay Sols

Clay sols are negatively charged and are usually flocculated by low concentrations of neutral salts. The valency rule may apply fairly well at least for certain sols. Hall and Mouson,[60] for example, determined the precipitation values of various chlorides, sulfates, and nitrates on a clay sol and found the order of cations to be: H, Al > Ca, Ba, Mg > K > Na; and the stabilizing power of the anions to be: $OH > SO_4 > NO_3 > Cl$.[61] Bradfield[62] showed, however, that the valency rule can have no general validity since the flocculation value may vary widely

[57] *Cf* Asch and Asch· "The Silicates in Chemistry and Commerce," London

[58] Van Bemmelen's "Godenboek," 163 (1910); Biedermann and Herzfeld: Rics' "Clays," 123 (1914); Cook: N. J. Geol. Survey, 287 (1878); Vogt: Compt. rend., **110**, 1199 (1899); Haworth: Mo. Geol. Survey, **11**, 104; Wheeler: 106 (1896).

[59] Private communication.

[60] J. Agr. Sci., **2**, 251 (1907).

[61] *Cf.* Kermack and Williamson: Proc. Roy. Soc. Edinburgh, **45**, 59 (1925).

[62] Soil Sci., **17**, 411 (1924).

with slight changes in (1) hydrogen ion concentration, (2) concentration of sol, and (3) nature of the exchangeable cations. The important findings of Bradfield have been confirmed and extended by Wiegner,[63] Baver,[64] Mattson,[65] and especially by Jenny and Reitemeier,[66] whose work will be considered in some detail.

ζ-potential, Exchange, and Flocculation Data for Clay Sols. The migration velocity, μ, of the particles of various clay sols prepared from natural Putnam clays (*cf.* p. 391) was measured with an ultramicroscope in an open cataphoresis cell and the ζ-potential in millivolts calculated from the average of a number of measurements, using the Freundlich equation (p. 396). The percentage release of the cations from the multivalent clays was determined after treating with potassium chloride, and that of the univalent clays was calculated from exchange values with NH_4-clay. Since potassium and ammonium ions are equally well adsorbed and released, the data are comparable quantitatively. Flocculation values were obtained both from KCl and for MCl where M is the cation common to the clay. The data are given in Table LIV. The amount of electrolyte added to the system is expressed in terms of "symmetry values, S," that is, in multiples of the number of milliequivalents of adsorbed ions in the system. The magnitude of the exchange expressed in percentage of the symmetry concentration equal to one ($S = 1$) is called the symmetry value.

Effect of the Charge and Size of Adsorbed Cations on the ζ-potential. The influence of charge and size of the adsorbed cations on the ζ-potential of clay particles is shown graphically in Fig. 67 from Jenny and Reitemeier's data (Table LIV). Comparing rare gas type ions of equal size, the potential tends to be lower as the valence of the ion is higher. The comparison must be restricted to ions of equal size since certain uni-clays (*e g*, Cs-clay) have lower potentials than some of the bi-clays (*e g.*, Mg-clay). Comparing rare gas type ions of equal valency, the ζ-potential is higher the smaller the adsorbed cation. This agrees with Wiegner's view that the most highly hydrated ions (in general small ions are strongly hydrated) cause the highest ζ-potential.

ζ-potential and Ionic Exchange. Jenny visualizes clay particles as plate-shaped crystals which hold adsorbed ions on their surfaces. Because of heat motion and Brownian movement, the ions are not at rest but oscillate (p. 397) and, at some times, may be a considerable dis-

[63] Kolloid-Z. (Zsigmondy Festschrift), **36**, 341 (1925).
[64] Baver. Mo. Agr. Expt. Sta. Research Bull 129 (1929)
[65] Mattson: Soil Sci, **28**, 179, 221 (1929).
[66] J. Phys. Chem., **39**, 593 (1935).

tance from the wall. The cation of an added electrolyte may slip between the negative wall and the positive oscillating ion, the former becoming adsorbed and the latter remaining in solution as an ex-

TABLE LIV

ζ-POTENTIALS, EXCHANGE ADSORPTION, AND FLOCCULATION OF CLAYS

Sol	μ	Temp. °C	ζ (millivolts)	%-release (symmetry values)	Flocculation values S-concentrations	
					KCl	MCl
Li-clay ...	3 45	30 3	58 8	68 0	21 6	26 0
Na-clay ..	3 41	28 9	57 6	66 5	11 2	14 8
K-clay. . .			56 4	48 7	7 8	7 8
NH_4-clay	3 48	33 2	56 0	50 0	5 4	4 9
Rb-clay ..	3 25	30 3	54 9	37 4		
Cs-clay	3.02	30 3	51 2	31 2	5 6	4 2
H-clay ..	2 84	30 3	48 4	14.5	1 5	0 36
Mg-clay	3 18	30 3	53 9	31 32	2 9	0 69
Ca-clay	3 27	32 8	52 6	28 80	3 0	0 55
Sr-clay . ..	3 06	30 3	51 8	25 76	2 6	
Ba-clay. . ..	3 01	30 3	50 8	26 75	2 3	
La-clay	2.74	21 2	45 5	13 96	0 86	. .
Th-clay...	3 11	32 2	50 4 47 1	1 85	0.60	..
M.B.*-clay.....	2 57	33 7	40 5		0 0	...

* Methylene blue

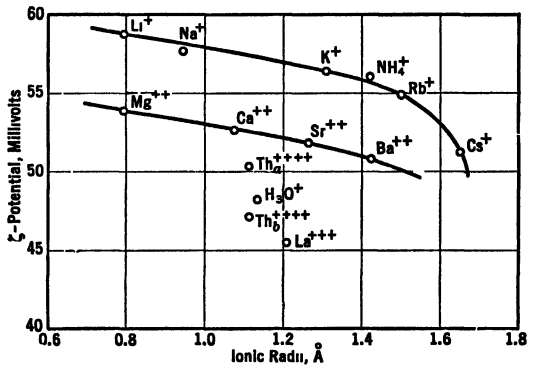


FIG. 67.—Effect of charge and size of adsorbed cations on the ζ-potential of colloidal clay particles.

changed ion. From this point of view, the more loosely an ion is held, the greater the average distance of oscillation and the greater the likelihood of replacement; and conversely, the more closely the cation sticks to the surface, the less readily will it be replaced. Since the average distance of oscillation corresponds directly to the average thickness of the double layer, it would follow that clays with high ζ-potentials should have adsorbed ions which are easily exchangeable. A comparison of the ζ-potential with the percentage release of adsorbed ions (columns 4 and 5 of Table LIV) supports this deduction. Since thorium is so difficult to replace, it is probable that the observed ζ-potential of Th-clay is much too high.

ζ-potential and Flocculation Values. The close relationship between ζ-potential and flocculation value is again illustrated by the data of Table LIV shown graphically in Fig. 68 in which the precipitation

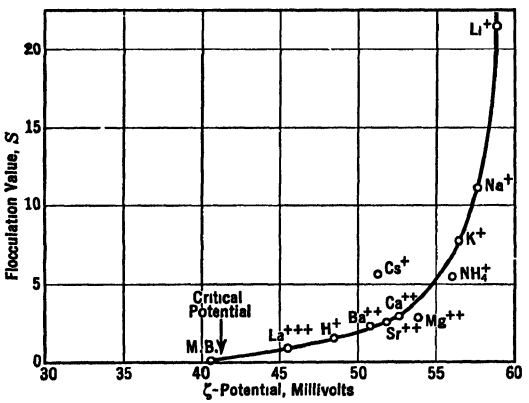


FIG 68.—Flocculation values of uni- and poly-clays by potassium chloride

values of potassium chloride are plotted against the ζ-potential. Obviously, it takes much more electrolyte to coagulate a clay with a high ζ-potential than one with a low potential. The curve cuts the x-axis well above zero in accord with Powis' concept of a critical potential for flocculation (p. 181). For the systems under consideration the value appears to be 42 millivolts. That this value must be approximately correct is evidenced by the behavior of methylene blue clay which has a potential of 40.5 millivolts and therefore flocculates completely without the addition of electrolyte.

Flocculation Values and Exchange Adsorption. The flocculation values, F, and exchange adsorption values, E, of various electrolytes

for three different clays are given in Table LV, after Jenny and Reitemeier. Both values are expressed in symmetry values S (p. 417). With the exception of H^+ ion, the valency rule applies, but only in the sense that the ion with the highest valence precipitates in the lowest concentration. Ions of the same valence, especially univalent ions, show a wide variation in precipitation value. Whenever the flocculating electrolyte contains a foreign cation, exchange adsorption always takes

TABLE LV

RELATION BETWEEN FLOCCULATION VALUES OF ELECTROLYTES AND EXCHANGE ADSORPTION

Electrolyte	NH_4-clay		Ca-clay		H-clay	
	F (S)	E (S)	F (S)	E (S)	F (S)	E (S)
LiCl	8 0	32 0	4 8	13 08	2 9	6 6
NaCl.	8 0	33 5	4 5	12 74	2 7	6 2
KCl.	5 4	51 33	3 0	28 80	1 5	14 5
NH_4Cl .	4 9	50	2 5	29 35	1 3	
RbCl.	4 7	62 56	1 87	43 85	1 17	28 20
CsCl . .	2 8	68 78	1 17	50 83	0 73	39 73
HCl	0 98	84 89	0 55	77 80	0 36	50
$MgCl_2$.	1 22	65 44	0 59	47 53	0 47	15 78
$CaCl_2$	1 27	63 56	0 55	50	0 47	26 89
$BaCl_2$	1 16	71 67	0 55	52 96	0 35	23 78
$La(NO_3)_3$	0 90		0 47		0 18	
$ThCl_4$..	0 75	80 89	0 36	80 24	0 16	

place. Comparing the flocculation and ionic exchange data of Table LV, it appears that those ions which are weakly adsorbed have high flocculation values, whereas ions which are taken up strongly by exchange, precipitate in low concentrations. This may be shown graphically by plotting the flocculating power F_p, which is the reciprocal of the flocculation value, against the exchange adsorbability, Fig. 69. The resulting curves may be represented by the empirical equations:

$$F_p = 0.140e^{-0.0332E} \text{ (for Ca-clay)}$$

$$F_p = 0.284e^{-0.0431E} \text{ (for H-clay)}$$

In other words, the coagulating effect of an ion increases exponentially with its exchange adsorbability. The position of the curves for the dif-

ferent clays emphasizes the fact that the flocculation value of a given cation is determined in large measure by the nature of the exchangeable ion initially present in the clay.

If the clay contains a highly hydrated univalent ion such as Na-clay, the ζ-potential is high since the ions are loosely bound and oscillate through considerable distances. This means that the effective width of the double layer is great or the degree of dissociation is high. The flocculation value of an electrolyte for such a clay varies widely with the properties of the coagulating ion. If it is highly hydrated and univalent, such as Li^+ ion, the extent of the exchange adsorption will be relatively small and the change in ζ-potential will be altered but

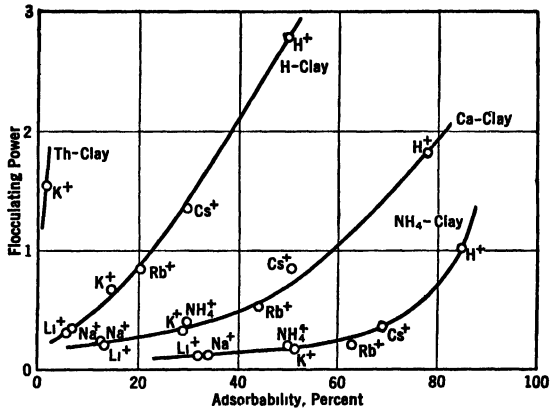


FIG. 69.—Relationship between the exchange adsorbability of univalent ions and their coagulating power for clays

little. The necessary lowering of the potential will be produced by a decrease in thickness of the double layer or a decrease in dissociation,[65] which requires large amounts of electrolyte (15–20 *S*). On the other hand, if the precipitating ion is univalent but not hydrated, such as Cs^+ ion, exchange adsorption predominates strongly, giving the particle a new outer layer which is so strongly attracted by the inner layer that the ζ-potential drops sharply. Very little electrolyte is required to repress the new outer layer to the critical distance characteristic of the critical potential; hence the flocculation values are small, of the order of 1 *S*.

Now if the original clay contains non-hydrated univalent ions such as lithium, or polyvalent ions such as thorium, the ζ-potential is low to

begin with. The addition of an electrolyte such as lithium chloride will produce a small exchange which will tend to increase the thickness of the double layer and thus raise the ζ-potential.[67] The peptizing action is finally overbalanced by the repressing effect of more electrolyte, and flocculation results with concentrations of medium magnitude (2–10 *S*) but somewhat higher than the common ion values. Finally, if the coagulating ion is similar in nature to the one on the clay originally, ionic exchange again assumes greater proportions without greatly modifying the ζ-potential. Flocculation is occasioned chiefly by the necessary decrease in dissociation at low electrolyte concentrations, often less than 1 *S*.

In the flocculation of acid clay sols with bases, the first step in the process is the neutralization of the acid followed by the coagulation of the resulting clay salt. The precipitation value of salt-base mixtures such as KCl-KOH and $CaCl_2$-$Ca(OH)_2$ involves not only the coagulating action of the cation but also the neutralizing and peptizing influence of hydroxyl ion.[68]

Deflocculation of Clays

The colloidal matter of a soft clay is deflocculated on shaking with water but the process is greatly facilitated by the presence of electrolytes with strongly adsorbed anions such as alkali hydroxide, carbonate, and silicate; and is retarded or prevented by electrolytes with strongly adsorbed cations. The deflocculating power of calcium hydroxide is less marked than that of the alkali hydroxides because of the relatively strong precipitating action of calcium ion.[69] Comber[70] attributes the abnormal flocculating power of calcium hydroxide above a certain concentration to its coagulating action on emulsoid matter such as silica that has a stabilizing action on the clay sol.[71] Clays which contain appreciable amounts of soluble salts, such as the sulfates of calcium and magnesium, are difficult to deflocculate because of the precipitating action of the cation. On the other hand, clays containing protecting colloids such as humus are easily deflocculated. In technical practice,

[67] *Cf.* Baver: Mo. Agr. Expt. Sta. Research Bull., 129 (1929).

[68] *Cf.* Bradfield: J. Phys. Chem., **32**, 202; Mattson: 1532 (1928); Oakley: Nature, **118**, 661 (1926).

[69] *Cf.* Joseph and Oakley: Nature, **117**, 624 (1926).

[70] J. Agr. Sci., **10**, 426 (1920); **11**, 450 (1921); **12**, 372 (1922); Nature, **118**, 412 (1926).

[71] *Cf., also,* Hardy: J. Phys. Chem., **30**, 254 (1926); Kermack and Williamson: Nature, **117**, 824 (1926); Proc. Roy. Soc. Edinburgh, **47**, 202 (1927).

tannin is sometimes added to facilitate the deflocculating action of the electrolytes and to increase the stability of the slip (p. 415).

The *p*H value at which clay particles attain a maximum charge is lower for sodium silicate solutions than for sodium hydroxide or

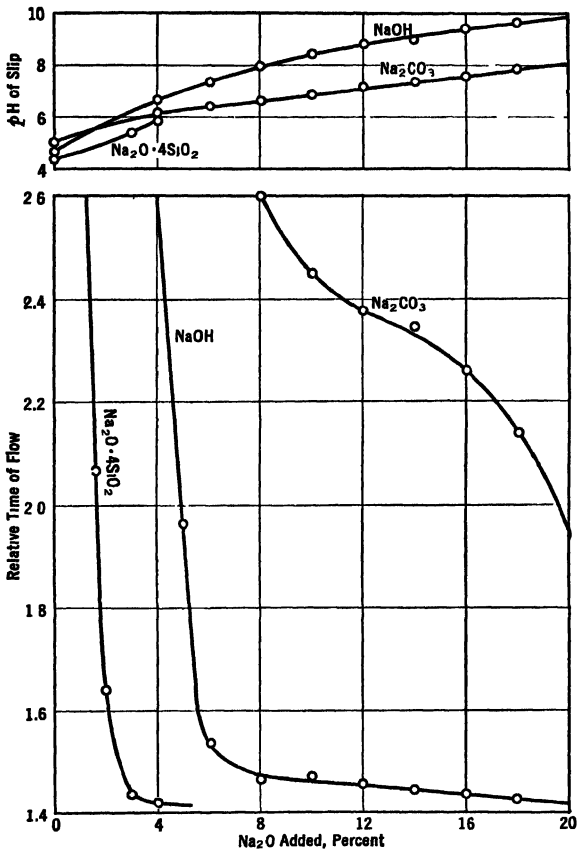


FIG. 70.—The action of deflocculating agents on a Florida kaolin.

sodium carbonate. This is illustrated by Fig. 70[72] in which the relative time of flow of a kaolin slip through an efflux viscosimeter is plotted against the sodium oxide content of the several deflocculating

[72] McDowell: J. Am. Ceram. Soc., **10**, 225 (1927).

solutions. The greater deflocculating action of the silicate solutions probably results from the presence of colloidal silica which adsorbs sodium ions, thus disturbing their equilibrium with the hydroxyl ions and allowing the hydroxyl ions to be adsorbed more readily by the clay particles than they would be from a sodium hydroxide or carbonate solution. It is therefore necessary to specify the deflocculating agent employed when giving the *p*H value at which a clay slip possesses its maximum fluidity. Silica sol alone does not serve as a deflocculating agent for clay.

Adsorption of Anions

The adsorption of univalent ions such as nitrate and chloride by soil colloids is relatively weak. Indeed Mattson[73] observed negative adsorption of various anions by clays in the order: $Cl = NO_3 < SO_4 < Fe(CN)_6^{----}$. This does not mean that none of the anions is adsorbed but only that the solvent is more strongly adsorbed than the anions. Actually, the adsorption of an anion such as nitrate is so weak that a nitrate fertilizer should be applied only as needed since any excess will be leached out by drainage water. Phosphate, on the other hand, is retained by the soil colloids under suitable conditions that have been summarized by Bradfield, Scarseth, and Steel:[74] At *p*H values from 2 to 5, the retention is attributed to the gradual dissolution of iron and aluminum and their reprecipitation as the phosphates. At *p*H 4.5 to 7.5, the phosphate appears to be adsorbed on the surface of the clay particles. The adsorption proceeds rapidly, and a fairly sharply defined saturation value is reached that is independent of the concentration of the added phosphate and seems to bear no relationship to the base-exchange capacity. At *p*H 6–10, no adsorption takes place unless bivalent cations such as calcium are present.[75] The bivalent cation may act by the formation of an insoluble phosphate or by increasing the adsorption of the anion, or both phenomena may enter in. The further possibility that phosphate ion replaces hydroxyl, silicate, or other groups from the surface of the aluminosilicate particle has not been excluded.

Chemical Reactions

The action of hydrogen clays with inorganic bases might be treated under base exchange, but since a definite chemical neutralization is

[73] Soil Sci., **28**, 179 (1929).

[74] Trans. Intern. Congr. Soil Sci, 3rd Congr., Oxford, **1**, 74 (1935).

[75] *Cf.* van Bemmelen: "Die Absorption" (1910); Rostworowski and Wiegner. J. Landw., **60**, 223 (1912).

involved it seems better to consider such processes under the heading of chemical reactions.

By prolonged electrodialysis of a clay, practically all the exchangeable bases are removed and all soluble acids whose anions are capable of passing a parchment membrane are taken out. If such a "hydrogen saturated" clay is allowed to deposit on the anode membrane, the paste may have a *p*H value of 2–3.5 whereas the clear water in which it was dispersed may be almost neutral. The *p*H value of such clay acids

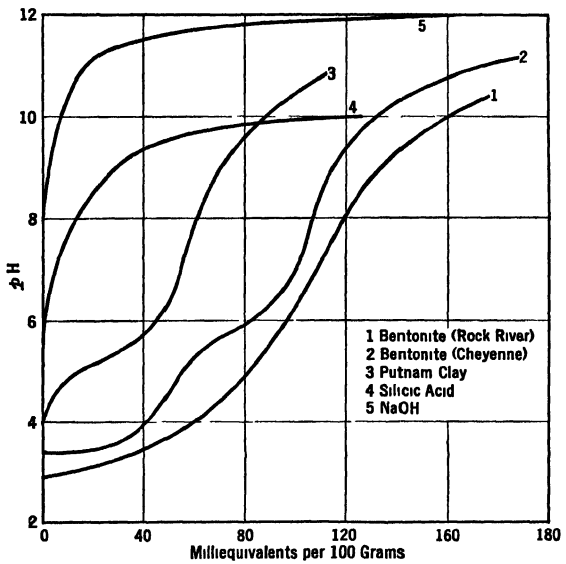


FIG 71.—Typical titration curves for electrodialyzed colloidal clays.

varies with the sol concentration in much the same way as that of a weak acid, like acetic, varies with the concentration.[76]

Titration of Clay Acids. Bradfield has titrated electrodialyzed clay acids by means of the hydrogen electrode[77] and the glass electrode.[78] Some typical curves obtained by titrating 100 cc of the clay sols with 0.1 *N* NaOH are shown in Fig. 71, together with the curve

[76] Bradfield. J. Phys. Chem., **28**, 170 (1924)

[77] Bradfield. Proc 1st Intern Congr. Soil Sci., **4**, 858 (1927); J. Phys. Chem., **28**, 170 (1924); **35**, 367 (1931); Colloid Symposium Monograph, **8**, 367 (1931).

[78] Naftel, Schollenberger, and Bradfield. Soil Research, **3**, 222 (1933).

for electrodialyzed silicic acid. It is apparent that the silicic acid is much weaker than the clay acids; the former exhibit practically no buffer action whereas the latter are usually well buffered at $pH = 5$–6.5 and hence are of about the same strength as the first hydrogen of carbonic acid. Comparing the apparent dissociation constants, pK, of silicic acid and a typical clay acid on the basis of the mass law equation: $p\text{H} = p\text{K} + \log \text{salt/acid}$, at the point where the acid is half neutralized (*i e*, where $p\text{H} = p\text{K}$), it is found that the pK value of silicic acid is 10–11 in agreement with the accepted values whereas the "apparent pK" value of Putnam lay is 5.6; of Rock River bentonite 3.8; and of Cheyenne bentonite, 3.6 and 5.9. The term "apparent pK value" was used since in the above treatment it was assumed that the clay behaves as a simple monobasic acid giving only one break, whereas it is probably a complicated polybasic acid the hydrogen ions of which, in different positions and possibly in different groupings on the surface of the colloidal particle, have somewhat different dissociation tendencies. However, the majority of them seem to have values of the same order of magnitude as a simple acid having a pK value approximately that of the apparent pK value. One complicating condition is that the apparent pK value obtained from titration curves is influenced noticeably by the nature of the base employed.[64]

The neutralization of the exchangeable hydrogen in clays is about complete at pH values varying from about 7.5 with calcium, barium, and magnesium hydroxides to 8.5 with sodium and lithium hydroxides. At higher pH values, the aluminosilicate minerals are decomposed to a certain extent, forming simpler aluminates and silicates. The resulting alkali decomposition products are either in molecular solution or approach the molecular state of subdivision whereas the alkaline-earth compounds are less highly dispersed than the alkali compounds but are finer than the original clay.[79]

[79] *Cf* Bradfield: Alexander's "Colloid Chemistry," **3**, 581 (1931).

CHAPTER XXIII

CEMENT

The term cement, as ordinarily used at the present time, refers to mortars which possess the property of hardening in water as well as in air. Attention has already been given to plaster of Paris (p 61) and to hydraulic mortars in which magnesia or zinc oxide is the most important constituent (Vol. II, pp. 183, 189). This chapter will deal with Portland cement and related products.

PORTLAND CEMENT

The need for a cementing material to bind sand and small stones together was ecognized from the time man started to build. In some of their constructions, the Assyrians and Babylonians are known to have used moistened clay which was probably the first cementing material ever used for building purposes. Such a binder is not sufficiently durable or hard for building massive structures, and the next development appears to have been the discovery by the Egyptians of the cement now known as plaster of Paris, which was mixed with sand to make the mortar used in the construction of the Pyramids. The discovery that the application of heat to certain rock minerals, such as gypsum, would give a cementing substance was later utilized by the Greeks in making lime from limestone or marble. The Greeks prepared some very satisfactory mortars by mixing lime with sand and volcanic earths known as pozzolana. The development of pozzolana mortars was brought to a high state of perfection by the Romans, as evidenced by many of their imposing structures which still exist. The so-called Roman or pozzolana cements were similar in many respects to the modern Portland cement.

The art of cement making declined with the fall of Rome and was not advanced until 1756 when John Smeaton discovered that a clayey limestone found in Cornwall would give a hydraulic lime, when burned. This product was mixed with pozzolana to prepare the mortar used in constructing the Eddystone lighthouse. Because of the scarcity of

pozzolana, which is found only in a few volcanic regions, subsequent investigations were carried out in an attempt to produce an artificial Roman cement. The invention of a satisfactory process is attributed to Joseph Aspdin of Leeds, who took out a patent in 1824 for making a cement by heating an intimate mixture of limestone and clay at the temperature ordinarily used in burning lime. It had been the custom in preparing limes to heat argillaceous limestones in a stack furnace under conditions such that some parts of the charge were sintered. These sintered lumps were discarded because they were difficult to grind. Aspdin, however, ground some of them and found the resulting powder to possess superior cementing properties. To this product, Aspdin gave the name Portland cement, since its color, after hardening, was similar to that of Portland stone, a famous English building stone. Aspdin's original cement was not what is now known as Portland cement, since the temperature of burning was not high enough; but a year later, in 1825, the importance of heating the mass to incipient fusion was recognized. From this beginning, more than a century ago, there has developed the modern Portland cement industry.

The importance of Portland cement in our present-day civilization is difficult to overestimate. Starting with the turn of the century, the industry began to grow by leaps and bounds until in the year 1936 one hundred million barrels of cement were manufactured. This vast production is occasioned by the diversity of its important applications chiefly in the form of concrete, a mixture of cement, gravel, and sand. The importance of concrete construction reveals itself in no more striking way than in the interlacing ribbon of rock which constitutes the vast highway system. Concrete roads, including the bridges, tunnels, and reinforced embankments, have made possible the full utilization of the automobile in communication and in transportation. Moreover, concrete, the ideal plastic rock, has found application in the fabricating of all kinds of structures from small homes to massive buildings, and gigantic monoliths such as Boulder Dam. The strength and rigidity of reinforced-concrete buildings provides safety from such destructive agencies as earthquake, fire, and tornado, which have leveled less sturdy forms of construction. Nor need beauty be sacrificed to utility in modern concrete fabrication. An outstanding example of artistry in concrete is the magnificent Baha'i temple in Chicago, the dome of which is "a shelter of cobweb interposed between earth and sky, struck through and through with light."[1] This building was done by Earley,

[1] *Cf.* Bogue: Ind Eng. Chem., **27**, 1312 (1935).

who also made one of the first great statues from concrete, Lorado Taft's "Fountain of Time" in Chicago.

Much of the progress in the utilization of cement has been made possible by the investigations of scientists into the constitution of the material and the properties of its individual components. Because of the application of this knowledge it is no longer necessary to cure a concrete slab 21 days before use; a concrete road may now be made which may be safely opened to traffic two to three days after laying. Modern research has likewise improved the volume constancy of concrete and has thereby minimized the cracking and crazing of structures. Moreover, the scientist has shown how a cement may be manufactured which is resistant to the attack of sulfates and sea water. Finally, Portland cement with a low heat of hydration has been developed which enables the engineer to pour rapidly huge volumes of concrete without the generation of so much heat within the mass that cracks develop on cooling. Boulder Dam was made possible as a result of this scientific achievement.

The importance of scientific investigations on this highly practical material is emphasized by Bogue,[1] as follows: "Research on Portland cement and concrete has enabled the engineer to design structures with greater assurance of durability, of security, and of a wider field of usefulness. It has placed in the hands of the architect a material with which he may fabricate the most massive monoliths or which he may mold into the most delicate tracery of ornamentation and to which he may impart any tone or tint of the rainbow. It has had an important part in the development of an incomparable network of highways, great and inspiring edifices, and economical homes which are durable and secure abodes of lasting beauty. Thus has research upon Portland cement contributed, in this industrial age, to the satisfaction of life." It is to an account of some of the most important scientific results of this research that attention will now be given.

Manufacture

Portland cement is produced by heating a mixture of rock-forming materials containing suitable amounts of aluminum, calcium, and silicon together with small amounts of iron and magnesium. In the early stages of the development of the industry, the method of procedure employed in making a satisfactory cement was determined by the method of trial and error. Now, it is known that certain definite compounds impart the desired properties to cement and that a uniform

product made up of these compounds results only when the raw material containing calcium, aluminum, and silicon in rather definite proportions is ground to a fine powder and the very intimate mixture heated to a minimum temperature.

Typical raw materials employed in cement manufacture are limestone and clay, both of which are found in large deposits of uniform composition. In some places, there exist deposits of clayey limestone, called cement rock, containing all three of the essential constituents; but, as a rule, either limestone or clay must be added to get the desired composition for good Portland cement. The alumina and silica are sometimes derived from blast-furnace slag and the calcium oxide from sea shells. From whatever source the material is obtained, the separate constituents are mixed in the proper proportions and thoroughly pulverized. If the raw materials are rocks, the grinding is commonly carried out in the dry way. On the other hand, soft materials, such as marl and clayey mud which are gathered by dredging operations, are usually ground wet and are kept suspended until dried out in the kiln.

The burning process is carried out in cylindrical kilns, 100 to 400 feet in length and 6 to 12 feet in diameter, built of steel plates and lined with highly refractory material. The drums are held in a slightly inclined position by friction rollers and are rotated slowly. The process is continuous, the raw mix entering at one end of the kiln and the cement clinker leaving it at the other. The heat is derived from pulverized coal, fuel oil, or gas which are blown into the lower end of the kiln by compressed air, giving a flame 15 to 40 feet in length. The time of passage through the kiln is from 1.5 to 3 hours, during which the raw material is subjected to a gradually increasing temperature that reaches a maximum of 1425 to 1500°. In the first stage of the burning process, the raw material is thoroughly dried; in the second stage, carbon dioxide and organic matter are driven off; and in the final stage, the alumina, silica, and lime react to form the cement clinker. The clinker consists of partially sintered masses of particles from 0.5 to 6 cm in diameter. After the addition of a small amount of gypsum which regulates the rate of setting, the particles of clinker are ground to a fine powder, the surface area of which ranges from about 1400 to 1900 cm^2/g; this is the Portland cement of commerce.

Ordinary Portland cement prepared as described above hardens rather slowly, ten days or more being required for a concrete slab to cure properly. Rapid-hardening Portland cement is now prepared in much the same manner as the ordinary product except that the proportion of lime may be increased somewhat, the raw materials are more

carefully mixed and ground, the burning is carried out at a somewhat higher temperature, and the clinker is much more finely ground. The rapid-hardening cement contains more tricalcium silicate (p. 438) than the ordinary cement.

Composition and Constitution

Composition

The results of the analysis of a few typical cements are given in the left-hand portion of Table LVI. Small amounts of K_2O and

TABLE LVI

Composition and Constitution of Some Typical Cements

Type of cement	Composition—per cent						Free CaO	Constitution—per cent			
	CaO	MgO	Al_2O_3	Fe_2O_3	SiO_2	SO_3		C_4AF	C_3A	C_3S	C_2S
Ordinary Portland	63 9	2 5	5 8	2 9	21 1	1 7	0 8	9	10	52	21
Rapid-hardening Portland	64 5	2 3	6 0	2 8	20 0	2 3	1 5	9	11	60	12
White Portland	64 7	0 9	4 2	0 4	23 5	1 9	1 5	1	10	44	34
Iron ore or Erz	64 8	0 7	1 7	8 2	23 3	1 1					
Portland-blast furnace	60 2	3 5	7 5	1 4	22 6	1 3					
Eisen-Portland	46 8	2.2 (FeO)	8 0	2 7	31 6	2 3	0 6 TiO_2				
Aluminous	40 1	7 7	37 5	5 6	6 6	0 6	2 0				

Na_2O are also present in most cements. The analysis gives, of course, only the percentage amounts of the several components and does not indicate the nature of the compounds.

Since more than 90% of the average Portland cement consists of calcium, aluminum, and silicon, referred to the oxides, it is reasonable to suppose that its properties result chiefly from compounds of these three constituents. As a matter of fact, Richardson [2] demonstrated that a good Portland cement can be made by starting with lime, silica, and alumina in the pure state.

Constitution

Many workers have been concerned with the constitution of Portland cement since Le Chatelier [3] published the results of his classical investigations more than a half-century ago. In most of the work,

[2] Cement, **5**, 314 (1904).

[3] "Experimental Researches on the Constitution of Hydraulic Mortars" (1887), translated by Hall (1905).

the evidence offered in support of the alleged reactions which take place during the burning process, and of the compounds formed, is not convincing since the criteria used to define a compound were either indefinite or insufficient. The solution of many questions connected with the constitution and setting of Portland cement has been brought about by the thorough systematic investigations carried out in the Geophysical Laboratory and the National Bureau of Standards. Rankin and Wright[4] in their pioneer work in 1915 made a complete phase-rule study of the ternary system CaO-Al_2O_3-SiO_2 which necessitated the investigation of about 1000 different compositions and fully 7000

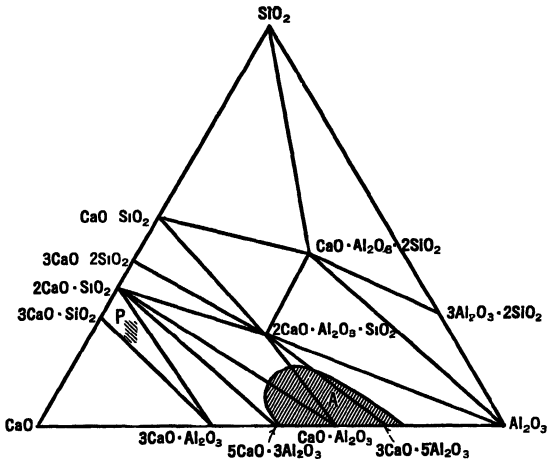


FIG 72.—Final products of the crystallization of lime, alumina, and silica. *P* is the Portland cement zone and *A*, the aluminous cement zone.

heat treatments and microscopical examinations. The results of these observations are summarized in the triangular concentration diagram shown in Fig. 72. In this diagram, the pure components are represented by the apexes of the triangle; the binary mixtures, CaO-Al_2O_3, Al_2O_3-SiO_2, and SiO_2-CaO, respectively, by points on the three sides; and ternary mixtures, by points within the triangle. Each side of the triangle is divided into 100 parts, and all compositions are given as percentage weights of the components. The lines within the large triangle divide it into 14 small triangular spaces which enclose all possible mixtures of the three components whose compositions are

[4] Am. J. Sci., (4) **39**, 1 (1915); Shepherd, Rankin, and Wright: Ind. Eng. Chem., **3**, 211 (1911); Rankin: **7**, 466 (1915).

represented by the apexes of the respective triangles. The region of Portland cement falls in the shaded area within the triangle which indicates the three solid phases at equilibrium to be tricalcium silicate, dicalcium silicate, and tricalcium aluminate.

Since Portland cement contains other components than lime, alumina, and silica, phase-rule studies had to be made of systems other than CaO-Al_2O_3-SiO_2. Among those which have received special consideration are systems containing the components MgO,[5] Fe_2O_3,[6] K_2O,[7] and Na_2O.[8] The results of these comprehensive studies indicate with considerable certainty that Portland cement under equilibrium conditions consists chiefly of $3CaO \cdot SiO_2$, $2CaO \cdot SiO_2$, $3CaO \cdot Al_2O_3$, $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$, and MgO.

In opposition to the above conclusion it has been claimed: (1) that the lime in excess of that necessary to form dicalcium silicate with the silica enters into solid solution with the dicalcium silicate;[9] (2) that $3CaO \cdot SiO_2$ does not exist, and that the chief constituent of clinker is $8CaO \cdot Al_2O_3 \cdot 2SiO_2$;[10] (3) that $3CaO \cdot Al_2O_3$ forms a solid solution with the silicates;[11] (4) that the clinker contains relatively large amounts of uncombined lime.[12] These views have been found untenable; and the results of phase equilibria, chemical, and microscopical studies have been confirmed in all essential respects by the application of x-ray analysis technique to the problem.[13] Taken together, the results indicate: (1) that the most abundant constituents of Portland cement clinker are $3CaO \cdot SiO_2$ and β-$2CaO\ SiO_2$; (2) that, in addition, the following compounds are normally present: $3CaO \cdot Al_2O_3$, $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$, and MgO; and (3) that free CaO is not normally present in amounts as great as 2.5%.

Bogue[14] has shown that it is possible to calculate the approximate equilibrium constitution of a Portland cement clinker from the oxide

[5] Rankin and Merwin: J. Am. Chem. Soc., **38**, 568 (1916); Am J. Sci., (4) **45**, 301 (1918); Ferguson and Merwin: **48**, 81 (1919); Hansen and Brownmiller. (5) **15**, 225 (1928); Hansen: J. Am Chem. Soc., **50**, 2155 (1928).

[6] Hansen and Bogue: J. Am. Chem. Soc., **48**, 1261 (1926); Hansen, Brownmiller, and Bogue: **50**, 396 (1928); Lea and Parker: Trans. Roy. Soc. (London), **234A**, 1 (1934).

[7] Brownmiller: Am. J. Sci., (5) **29**, 260 (1935).

[8] Brownmiller and Bogue: Am. J. Sci., (5) **23**, 501 (1932).

[9] Dyckerhoff: Zement, **16**, 731 (1927).

[10] Janecke: Z. angew. Chem., **74**, 428 (1912).

[11] Kühl: Zement, **13**, 512 (1924).

[12] Nacken: Zement, **16**, 1017 (1927).

[13] Brownmiller and Bogue: Am. J. Sci., (5) **20**, 241 (1930).

[14] Ind. Eng. Chem., Anal. Ed., **1**, 192 (1929).

and free lime analysis. The calculated constitution of some typical cements is given in the right-hand portion of Table LVI. In this table $C_4AF = 4CaO \cdot Al_2O_3 \cdot Fe_2O_3$; $C_3A = 3CaO \cdot Al_2O_3$; $C_3S = 3CaO \cdot SiO_2$; and $C_2S = 2CaO \cdot SiO_2$.

It must be emphasized that the above statements concerning the constitution of cement refer to equilibrium conditions only. Lea and Parker [15] and Dahl [16] have pointed out the possibility and outlined the results of disequilibrium conditions during the cooling of the clinker. For example, some of the liquid formed during clinkering which amounts to 25–30% may solidify as undercooled liquid or glass.[17] In the same connection, Insley [18] and Schwiete and Bussem [19] have observed by x-ray and optical methods that detectable and sometimes important amounts of other materials may be present in solid solution in the principal constituents; and Insley found by a petrographic analysis of commercial clinker that the relative amounts of the compounds, as observed by that method, may differ widely from the amounts calculated from chemical analysis according to Bogue's method. Moreover, in a study of the solidus and liquidus relations in the area CaO-$4CaO \cdot Al_2O_3 \cdot Fe_2O_3$-$CaO \cdot Al_2O_3$, McMurdie [20] found that $3CaO \cdot Al_2O_3$, $5CaO \cdot 3Al_2O_3$, and $CaO\ Al_2O_3$ all take Fe_2O_3 into solid solution up to 2.5%; and that $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$ takes up between 3 and 5% of the calcium aluminates into solution.

Setting and Hardening

When finely pulverized Portland cement is mixed with water, a plastic mass results which becomes solid in the course of a few hours. This process, which is called setting, is followed by a gradual increase in strength or hardening of the mass. Although ordinary Portland cement becomes very hard in the course of a week or ten days and the rapid-setting variety within a few days, the strengths may be increased over a period of years.

According to Le Chatelier,[3] the setting and hardening of Portland cement consists in the dissolution in water of the anhydrous silicates and aluminates, which subsequently become hydrated. Since the hydrates are less soluble than the anhydrous salts, the solutions become

[15] Dept Sci. Ind Research (Brit.), Build. Research Tech. Paper 16 (1935).
[16] Rock Products, **26** (Dec. 10, 1932).
[17] *See* McMurdie: J. Research Natl. Bur. Standards, **18**, 475 (1937).
[18] J. Research Natl. Bur. Standards, **17**, 353 (1936).
[19] Tonind-Ztg., **56**, 801 (1932).
[20] J Research Natl. Bur Standards, **18**, 475 (1937).

supersaturated with respect to the former and deposit an entangling mass of needles, thereby giving the cement its characteristic hardness. This theory of the hardening process was not questioned until Michaelis [21] recognized the formation not only of crystals but also of a gel which increased gradually in amount until it filled the interstices between the crystalline needles as well as those between the cement particles. The cementing gel was supposed to be calcium monosilicate, and the crystals tricalcium aluminate and calcium hydroxide. According to this hypothesis, the cement particles and crystals become embedded in a common sheath of gelatinous substance which imparts a degree of hardness that could not be attained by the felting of crystalline needles alone.

More or less successful attempts were made to distinguish the various products of hydration of Portland cement by the use of organic dyes which stain colloidal and zeolitic minerals selectively.[22] Such experiments led Blumenthal [23] to conclude that crystalline monocalcium silicate and tricalcium aluminate were among the first products of hydration and that a gelatinous silicate forms subsequently. Although this method of attack gave some helpful information, a systematic investigation of the setting and hardening process was possible only after the constitution of cement had been established. The essential constituents of cement being known, investigations were made by Klein, Phillips, and Bates [24] and by Rankin [25] of the action of water on each constituent in turn. These observations have been confirmed in most respects and extended by Lerch and Bogue,[26, 27] who investigated first the reactions of the cement compounds with an excess of water and later the behavior of the compounds both individually and collectively when mixed with water in proportions similar to those used with cements in concrete.

Action of Water on Portland Cement Compounds

Water added to dry Portland cement compounds is probably first adsorbed on the surface of the particles and later reacts either by

[21] Kolloid-Z., **5**, 9 (1909); **7**, 320 (1910); Chem.-Ztg., **17**, 982 (1893).

[22] Keisermann: Kolloid-Beihefte, **1**, 423 (1910).

[23] Silikat-Z., **2**, 43 (1914).

[24] Klein and Phillips: Bur. Standards, Tech. Paper 43 (1914); Bates and Klein: Tech. Paper 78 (1916); Phillips: J. Am. Ceram. Soc., **2**, 708 (1919).

[25] J. Franklin Inst., **181**, 747 (1916); Rankin and Wright: Am. J. Sci., (4) **39**, 1 (1915).

[26] Lerch and Bogue: J. Phys. Chem., **31**, 1627 (1927).

[27] Bogue and Lerch: Ind. Eng. Chem., **26**, 837 (1934).

hydrolysis or by hydration. The product of a hydrolytic reaction may take up water either by adsorption or in the form of a definite hydrate, and a definite hydrate may adsorb water giving a hydrous hydrate. In Fig. 73 [26] some observations on the amount of water fixed by adsorption or hydrate formation or both, calculated as percentages of the original anhydrous material, are plotted against time in days, for Portland cement compounds. The particles were ground to pass completely through a No. 100 sieve and 90% through a No. 200 sieve. In general, an amount of water equal to 50% of the weight of the cementing material was employed.

The compressive strengths of $^{15}/_{16}$ by 1 in. cylinders of the several compounds at ages up to 1 year are shown in Fig. 74.[27] The compressive strength is expressed in pounds per square inch. It is apparent from these curves that most of the compressive strength of Portland cement comes from the silicate constituents.

Tricalcium Aluminate. When $3CaO\ Al_2O_3$ is mixed with water, a gelatinous hydrous material is first formed which sets so rapidly that it is almost impossible to make test pieces. The rapid reaction is accompanied by a rise in temperature and loss of water as steam which favors the flash set. On adding more water and working rapidly, the paste does not again assume a rapid set. With limited amount of water in the paste, it is converted into and remains a submicroscopically crystalline gel during the first 24 hours at least; with more water, the microcrystals grow fairly rapidly; it never attains a high compressive strength. The final products of the hydration consist of fluffy isotropic aggregates of very fine crystalline grains having the composition $3CaO \cdot Al_2O_3 \cdot 6H_2O$,[28] with more or less adsorbed water. A hexagonal hydrate containing a larger amount of water may be formed at lower temperatures, but it tends to revert to the isotropic form. The isotropic grains of hexahydrate give a distinct x-ray diffraction pattern which contains none of the lines characteristic of anhydrous $3CaO \cdot Al_2O_3$, $5CaO \cdot 3Al_2O_3$, or $Ca(OH)_2$. Kühl and Thüring[29] claim that, when $3CaO \cdot Al_2O_3$ is hydrated in the presence of saturated calcium hydroxide, tetracalcium aluminate is formed, and Lafuma[30] concludes that hydrated tetracalcium aluminate and hydrated dicalcium aluminate result. Bogue and Lerch were unable to

[28] Thorvaldson, Grace, and Vigfusson: Can. J. Research, **1**, 36, 301 (1929); *cf.* Pulfrich and Linck: Kolloid-Z, **34**, 117 (1924); Duchez· Rock Products, **27**, No. 18, 62 (1924).

[29] Zement, **13**, 243 (1924); Roller: Ind. Eng. Chem, **26**, 669, 1077 (1934).

[30] Ciment, 174 (1925).

identify these new phases either by microscopic or x-ray methods in a mixture of tricalcium aluminate and 10% lime which was allowed to stand 2 years.

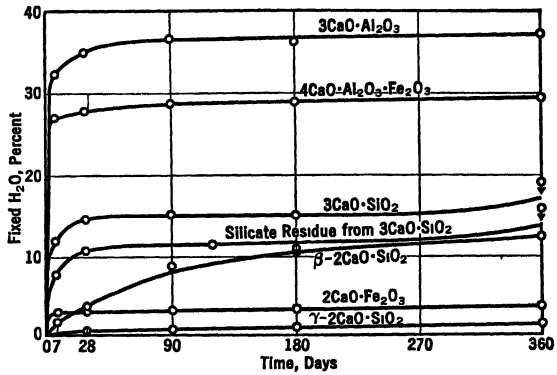


FIG 73—Water fixed by pure cement compounds after varying time intervals.

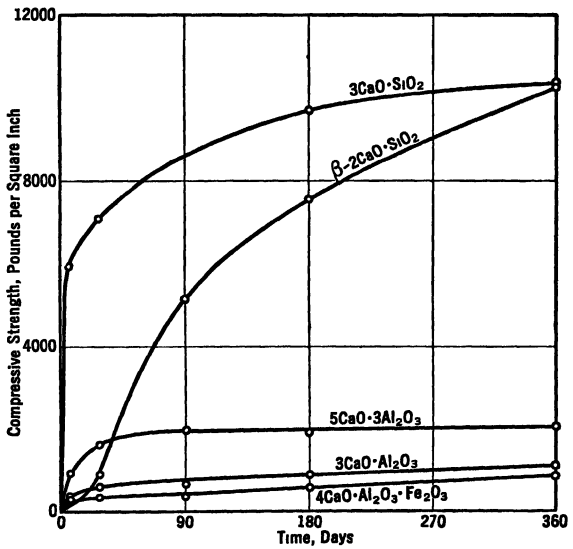


FIG. 74—Comparison of compressive strengths of cement compounds after varying time intervals.

Tricalcium aluminate mixed with the calcium silicates in the absence of a retarder tends to raise the early strength and lower the late

strength of the mixtures. Bogue and Lerch suggest that the effect of aluminate on the increase in early strength may be due to a decrease in the amount of water available to the $3CaO \cdot SiO_2$; and the later reduction in strength may be caused by the formation of tricalcium aluminate hydrate which gives an open structure and thereby prevents optimum contact of the hydrating calcium silicate granules.

Beta-dicalcium Silicate. β-$2CaO \cdot SiO_2$ takes up water very slowly. At the end of a month a slight etching accompanied by the formation of an amorphous layer around the edges was noted. The amount of this amorphous material increased gradually at the expense of the crystalline silicate, but a large amount of unhydrated material remained even after 2 years. Not more than a trace of calcium hydroxide could be detected, and no other new crystalline phase appeared. The actual amount of water bound was 0.7% at 1 day and 12% after 1 year.

γ-dicalcium silicate reacts much less rapidly even than the beta compound.

Tricalcium Silicate. $3CaO \cdot SiO_2$ is the only one of the three major constituents which reacts with water within a reasonable time to give a mass comparable to Portland cement in hardness and strength. In a paste containing 50% by weight of water, the compound was hydrolyzed to the extent of 15% (*i.e.*, the reaction $3CaO \cdot SiO_2 + xH_2O = 3Ca(OH)_2 + SiO_2\ xH_2O$ had proceeded 15% to completion), leaving an amorphous material of lower basicity than the original silicate. The hydrolysis had reached 23% in 7 days and 26% in 6 months; no further change was observed in 2 years. The silicate had fixed over 8% of water in 1 day and 19% at the end of a year (Fig. 73). Subtracting the water taken up as $Ca(OH)_2$ gives the water held by the $3CaO \cdot SiO_2$ residue. The hydrous hydrolysis products of both $3CaO \cdot SiO_2$ and $2CaO \cdot SiO_2$ appear to be entirely amorphous to x-rays when formed at ordinary temperatures.

The hydrolytic reactions of both silicates proceed more rapidly and further in an excess of water than in pastes that are allowed to set to a hard mass.[26, 27] The final decomposition product of $3CaO \cdot SiO_2$ in an excess of saturated limewater approaches the composition $3CaO \cdot 2SiO_2$ with a percentage hydrolysis of approximately 50. Assuming this to be the equilibrium composition, the $3CaO \cdot SiO_2$ paste under consideration hydrolyzed to but 53% of the equilibrium value in 2 years. In a similar way it was found that β-$CaO \cdot SiO_2$ pastes hydrolyzed to but 3.7% of the equilibrium value in 2 years.

The compressive strength developed by the calcium silicates in

Portland cement is probably caused chiefly by the gel of amorphous hydrous calcium silicate together with a felt of needle-like crystals of calcium hydroxide. Referring to Figs. 73 and 74 it will be seen that the increases in strength on aging are not proportional to the hydrolysis of the silicates since 2CaO SiO_2 hydrolyzes but little up to 1 to 2 years, yet it develops high strength in that time. Moreover, the strength increases are not proportional to the total combined water since neither calcium silicate shows any appreciable change in fixed water between 1 and 2 years whereas the strength, especially of the 2CaO SiO_2 mass, increases during that period. During earlier periods there is some correlation between the rate of development of strength and the water taken up by the two silicates. For Portland cements of widely varying composition, Lea and Jones [31] found a fair relation between the compressive strength of concrete and the water fixed in the set cement. The curve obtained by plotting combined water against the tensile strength is concave to the strength axis, indicating that the strength increases at a rate somewhat more than directly proportional to the amount of water taken up.

Tetracalcium Aluminum Ferrite. The compound 4CaO Al_2O_3 - Fe_2O_3 takes up water rapidly, giving a gelatinous impervious layer around the particles which retards the further penetration of the water. The compound fixed 25% of water in 1 day, increasing to 29% in 1 year (Fig. 73). A hydrolytic reaction takes place with the formation of a crystalline product which gives the same x-ray diffraction pattern as 3CaO Al_2O_3 $6H_2O$, and an amorphous product of unidentified constitution which Bogue and Lerch believe to be hydrous CaO · - Fe_2O_3. The compressive strength of the set compound is less even than that of 3CaO · Al_2O_3, and, when mixed with calcium silicates, the compressive strength of the mixtures is reduced.

Portland Cement. When water is added to Portland cement containing the four compounds considered above, the initial set results from the formation of a gel with 3CaO Al_2O_3 and to a certain extent with 4CaO · Al_2O_3 · Fe_2O_3. Pulfrich and Linck [32] emphasized the importance of gel formation in the initial set by showing that microscopically visible crystallization does not take place at the outset in the presence of the amount of water used in technical practice. Their observations were made in glycerol solutions in order to get the necessary dilution for microscopic examination, and the glycerol may have inhibited the crystallization. This, however, merely

[31] J. Soc. Chem. Ind., **54**, 63*T* (1935).
[32] Kolloid-Z., **34**, 117 (1924).

emphasizes the contention that setting is not necessarily occasioned by the formation of microscopically visible needles. The gel of tricalcium aluminate, which is largely responsible for the original set, reacts with water to give microscopic crystals of $3CaO \cdot Al_2O_3 \cdot 6H_2O$; and the gel from the ferrite gives ultimately both $3CaO \cdot Al_2O_3 \cdot 6H_2O$ and an amorphous ferrite, possibly $CaO \cdot Fe_2O_3$.

Whereas the initial set results primarily from the formation of tricalcium aluminate gel, the subsequent fairly rapid increase in cohesive strength and hardness is due in large measure to the hydration of $3CaO \cdot SiO_2$ and, to a lesser degree, of $2CaO \cdot SiO_2$ with the liberation of a calcium silicate gel in which are embedded needle crystals of calcium hydroxide. Rapid-hardening Portland cements contain more $3CaO \cdot SiO_2$ than the ordinary variety and are ground finer to allow more ready access of water. It is a pity that dicalcium silicate does not hydrate more rapidly since it is formed at a lower temperature than tricalcium silicate and yields ultimately a higher percentage of the important binding silicate gel.

To avoid overheating when enormous volumes of concrete are poured rapidly, as in the construction of Boulder Dam, it was necessary to develop a specification which placed definite limits on the computed compound constitution of the Portland cement, in order to ensure a low heat of hydration. These are as follows:[33] $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$ not over 20%; $3CaO \cdot Al_2O_3$ not over 7%; $2CaO \cdot SiO_2$ not over 65%: and $3CaO \cdot SiO_2$ not over 40%.

Action of Calcium Sulfate

As already pointed out in connection with the manufacture of Portland cement, gypsum is added in amounts up to 2–2.5% before grinding, in order to retard the time of set. The marked influence of gypsum is due largely to the removal of calcium aluminate as the insoluble calcium sulfoaluminate $3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 31H_2O$.[34] This delays the formation of the gel of $3CaO \cdot Al_2O_3 \cdot 6H_2O$ until all the sulfate is removed and so retards the initial set.

Gypsum also tends to counteract the effect of $3CaO \cdot Al_2O_3 \cdot 6H_2O$ in lowering the compressive strength of the calcium silicates. A pos-

[33] Robertson: Ind. Eng. Chem., **27**, 242 (1935).

[34] Kühl: Zement, **13**, 362 (1924); Lerch, Ashton, and Bogue: J. Research Natl. Bur. Standards, **2**, 715 (1929); Bogue and Lerch: Ind Eng. Chem., **26**, 837 (1934); *cf., however,* Klein and Phillips: Bur. Standards, Tech. Paper 43 (1914); Phillips: J. Am. Ceram. Soc., **2**, 708 (1919); Rohland: Kolloid-Z., **4**, 223 (1909); **8**, 251 (1911); Roller: Ind. Eng. Chem., **26**, 669, 1077 (1934)

sible explanation of this effect is that the structure of the set paste has time to be established by the reacting tricalcium silicate before any appreciable amount of $3CaO \cdot Al_2O_3 \cdot 6H_2O$, with its weak and open structure, can form.[35] Gypsum also counteracts the influence of $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$ in lowering the compressive strength of the calcium silicates. This effect may likewise be associated with the formation not only of calcium sulfoaluminate but also of calcium sulfoferrite, thereby cutting down the amount of amorphous hydrous ferrite that can be deposited on the calcium silicate granules.

Action of Other Salts

The addition of most salts influences the time of set to a greater or lesser degree, but the available data [36] are often conflicting. Some salts retard the set, and others accelerate it; another group of salts retards the rate of set when present in small amounts and accelerates it when larger amounts are used. Furthermore, the effect produced often varies with the composition of the cement employed. Gadd [36] investigated the action of a large number of compounds including the carbonate, nitrate, chloride, sulfate, borate, and hydroxide of sodium, ammonium, aluminum, zinc, cobalt, and chromium. He found that nitrates had little effect on the rate of set whereas all other compounds except gypsum and plaster of Paris accelerated it. In view of the influence of salts on jelly formation (Vol. II, p. 15), it is not surprising to find that their presence has an effect on the rate of set of cement, which may be altogether independent of any chemical action. One would expect the presence of foreign salts [37] to have a retarding or accelerating action depending on whether they have a coagulating or peptizing action on the colloids formed by the action of water on the cement particles.

Various mixtures are sold under trade names for accelerating the rate of set. These are composed of aqueous solutions of various salts such as carbonates, aluminates, silicates, or mixtures of various chlorides, such as those of calcium, aluminum, and sodium. One such accelerating material called "Cal" is prepared by the action of lime and calcium chloride in water. The accelerating action probably results from the

[35] Kuhl: Zement, **13**, 362 (1924).

[36] Gadd: Brit. Portland Cement Research Assoc, Pamphlets, 1 (1922); Thomas: Dept. Sci. Ind. Research (Brit.), Build. Research Special Rept. 14 (1929); Forsén: Zement, **19**, 1130 (1930); Biehl: **17**, 487 (1928).

[37] *Cf.* Benson, Newhall, and Tremper: Ind. Eng. Chem, **6**, 795 (1914).

precipitation of a calcium chloraluminate of the composition $3CaO \cdot Al_2O_3 \cdot CaCl_2 \cdot 18H_2O$,[38, 38] with an accompanying decrease in pH value. This reduction in pH accelerates the hydrolysis of the silicates and so hastens the hardening process. Platzmann,[39] on the other hand, attributes the action mainly to the hygroscopicity of calcium chloride which, by absorption of moisture during the first few weeks, prevents the shrinking and cracking of the cement and protects it from too rapid a loss of moisture.

IRON ORE AND PORTLAND BLAST-FURNACE CEMENTS

Iron ore or Erz cement is manufactured near Hamburg, Germany, in much the same way as ordinary Portland cement except that the clay or shale in the original mixture is replaced by iron ore. The ferric oxide content is relatively higher and the alumina relatively lower (Table LVI) than in ordinary cement; but the chief hydraulic constituent in both products is tricalcium silicate. The area occupied by cements rich in iron in a triaxial diagram of the system CaO-SiO_2-Fe_2O_3 is in nearly the same position as that of Portland cement in the system CaO-SiO_2-Al_2O_3.[40] Cements rich in iron contain $2CaO \cdot Fe_2O_3$ in addition to the four principal constituents of the ordinary product. This $2CaO \cdot Fe_2O_3$ is in solid solution with $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$.

Portland blast-furnace cement is a finely ground mixture of ordinary Portland cement clinker and granulated blast-furnace slag. The British standard specifications call for not less than 35% clinker nor more than 65% slag. In Germany two varieties of this type of cement are recognized by specification: Eisenportland cement containing not more than 30% granulated slag; and Hochoven cement containing not more than 85% granulated slag.

Portland blast-furnace cements are said to be superior for sea-water construction,[41] possibly because the added slag unites with any free lime, thereby preventing it from forming calcium hydrosilicates or from acting with the magnesium sulfate of sea water to give such compounds

[38] *Cf, however,* Kuhl and Ullrich: Zement, **14**, 859, 880, 898 (1925); Gassner: Chem.-Ztg, **48**, 157 (1924).

[39] Zement, **10**, 499 (1921); **11**, 137 (1922); Chimie & industrie, **7**, 943; **8**, 614 (1922).

[40] Kuhl · Zement, **10**, 361, 374 (1921).

[41] *For an account of the resistance of concrete to natural destructive agencies see* Lea and Desch: "The Chemistry of Cement and Concrete," 350 (1935).

as magnesium hydroxide[42] or calcium sulfoaluminate,[43] which are active in producing cracks. It is claimed that such cements resist the action of sulfates much more than ordinary Portland cement.[44] It is probable, however, that the chief importance of cements made with slag lies in the facility with which the waste product of an important industry is transformed into a commercially salable article. In any event, the present sulfate-resisting Portland cements which have a low content of 3CaO Al_2O_3 are quite as durable in sulfate waters as Portland blast-furnace cements.

ALUMINOUS CEMENT

Cements with a high alumina content were developed[45] because of the serious difficulties which were experienced in France owing to the decomposition of concretes in sea water and especially in earth containing large amounts of sulfates, chiefly gypsum. Cements in which the alumina content is equal to or greater than that of the silica content are known commercially as "aluminous," "fused," or "electrofused" cements. They are produced by fusion, because calcium aluminates soften readily, and clinkering is very difficult.[46]

The aluminous cement zone in the system CaO-Al_2O_3-SiO_2[47] is shown at *A* in Fig. 72. The compounds which may be present are therefore CaO Al_2O_3, $5CaO \cdot 3Al_2O_3$, $3CaO \cdot Al_2O_3$, $3CaO \cdot 5Al_2O_3$, 2CaO $Al_2O_3 \cdot SiO_2$, and 2CaO Si_1O_2. Of these we have seen that $3CaO \cdot Al_2O_3$ possesses slight hydraulic properties, and the same is true for $2CaO \cdot Al_2O_3 \cdot SiO_2$. $2CaO \cdot SiO_2$ is a good cementing material but develops strength slowly. Of the other compounds 5CaO - $3Al_2O_3$ sets very rapidly indeed, whereas both 3CaO $5Al_2O_3$ and $CaO \cdot Al_2O_3$ set slowly but harden rapidly developing great strength in 24 hours. The evidence indicates that $CaO \cdot Al_2O_3$ is by far the most important ingredient in aluminous cement; hence a pure aluminous cement should contain 35.45% CaO and 64.55% Al_2O_3, but the

[42] Lewis: Engineering, **109**, 626 (1920); Gary: Mitt. Materialprufungsamt, **37**, 12 (1919).

[43] Grun. Zement, **12**, 297, 307, 317, 326 (1924).

[44] Probst and Dorsch: Zement, **18**, 292, 338 (1929).

[45] *Cf* Bied: "Recherches industrielles sur les chaux, ciments et mortiers," Paris (1926).

[46] Bied: Tech moderne, **14**, 508 (1922); Rev. mét., **19**, 759 (1922)

[47] Bates: Bur. Standards Tech. Paper, 197 (1921); Endell: Zement, **8**, 319 (1919); Berl and Loblein: **15**, 642 (1926); Solacolu: **22**, 17, 33, 114, 191, 311 (1933); Kühl and Ideta: **20**, 261 (1931); Richter. **21**, 445 (1932).

commercial products vary in composition within 30–45% Al_2O_3, 35–45% CaO, 5–12% SiO_2, and 5–12% Fe_2O_3.

The reactions which take place in the setting and hardening of aluminous cements are still the subject of controversy. Le Chatelier,[48] Lafuma,[49] Kühl and Thüring,[50] and Koyanagi [51] are of the opinion that the hydration of aluminous cement can be represented essentially by the equation:

$$2(CaO \cdot Al_2O_3) + 10H_2O \rightarrow 2CaO \cdot Al_2O_3 \cdot 7H_2O + Al_2O_3 \cdot 3H_2O$$

Assarsson,[52] on the other hand, concludes from observations in the presence of limited amounts of water that the main reaction is the formation of monocalcium aluminate gel together with quite limited amounts of dicalcium aluminate and hydrous alumina. As in Portland cement, the ferric iron compounds doubtless give hydrous $CaO \cdot Fe_2O_3$.

As we have seen, the investigations which led to the production of aluminous cements were stimulated by the need for a product which was resistant to sulfur-bearing waters. These investigations were successful; under ordinary temperature conditions, aluminous cements resist the attack by sulfates and sea water to a greater extent than any other constructional cement with the possible exception of the sulfate-resisting Portland cements having a low $3CaO \cdot Al_2O_3$ content. Other advantages claimed for aluminous cements are greater earlier strength, and the higher temperature developed on setting, usually sufficient to allow normal hardening even in severe weather. Contrary to what is frequently reported, the chief advantage of aluminous cements is not their rapid hardening, which is equally characteristic of some Portland cements, but their marked resistance to chemical action.

Aluminous cements are now manufactured in many European countries, notably France and England; in the United States; and in French Indo-China. The chief drawback to their wide commercial use is the lack of a widely distributed supply of bauxite and the consequent high cost of raw material.

[48] Ciment, **32**, 82 (1927).
[49] "Recherches sur les aluminates de calcium," Paris (1932).
[50] Zement, **13**, 109, 243 (1924).
[51] Concrete, **40** (8), 40 (1932).
[52] Zement, **23**, 15 (1934).

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